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Seek simplicity, and distrust it.
-Alfred North Whitehead

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POLARIZATION and STATIC DIELECTRIC CONSTANT

The purposes of this chapter are (i) to develop equations relating the macroscopic properties (dielectric constant, density, etc.) with microscopic quantities such as the atomic radius and the dipole moment, (ii) to discuss the various mechanisms by which a dielectric is polarized when under the influence of a static electric field and (iii) to discuss the relation of the dielectric constant with the refractive index. The earliest equation relating the macroscopic and microscopic quantities leads to the so-called **Clausius-Mosotti** equation and it may be derived by the approach adopted in the previous chapter, i.e., finding an analytical solution of the electric field. This leads to the concept of the internal field which is higher than the applied field for all dielectrics except vacuum. The study of the various mechanisms responsible for polarizations lead to the **Debye equation** and **Onsager theory**. There are important modifications like Kirkwood theory which will be explained with sufficient details for practical applications. Methods of Applications of the formulas have been demonstrated by choosing relatively simple molecules without the necessity of advanced knowledge of chemistry.

A comprehensive list of formulas for the calculation of the dielectric constants is given and the special cases of heterogeneous media of several components and liquid mixtures are also presented.

2.1 POLARIZATION AND DIELECTRIC CONSTANT

Consider a vacuum capacitor consisting of a pair of parallel electrodes having an area of cross section $A \text{ m}^2$ and spaced $d \text{ m}$ apart. When a potential difference V is applied between the two electrodes, the electric field intensity at any point between the electrodes, perpendicular to the plates, neglecting the edge effects, is $E=V/d$. The

capacitance of the vacuum capacitor is $C_0 = \epsilon_0 A/d$ and the charge stored in the capacitor is

$$Q_0 = A\epsilon_0 E \quad (2.1)$$

in which ϵ_0 is the permittivity of free space.

If a homogeneous dielectric is introduced between the plates keeping the potential constant the charge stored is given by

$$Q = \epsilon_0 \epsilon A E \quad (2.2)$$

where ϵ is the dielectric constant of the material. Since ϵ is always greater than unity $Q_1 > Q$ and there is an increase in the stored charge given by

$$Q_1 - Q_0 = A E \epsilon_0 (\epsilon - 1) \quad (2.3)$$

This increase may be attributed to the appearance of charges on the dielectric surfaces. Negative charges appear on the surface opposite to the positive plate and vice-versa (Fig. 2.1)¹. This system of charges is apparently neutral and possesses a dipole moment

$$\mu = A E \epsilon_0 (\epsilon - 1) d \quad (2.4)$$

Since the volume of the dielectric is $v = Ad$ the dipole moment per unit volume is

$$P = \frac{\mu}{Ad} = E \epsilon_0 (\epsilon - 1) = \chi \epsilon_0 E \quad (2.5)$$

The quantity P , is the polarization of the dielectric and denotes the dipole moment per unit volume. It is expressed in C/m^2 . The constant $\chi = (\epsilon - 1)$ is called the susceptibility of the medium.

The flux density D defined by

$$D = \epsilon_0 \epsilon E \quad (2.6)$$

becomes, because of equation (2.5),

$$D = \epsilon_0 \epsilon E + P \quad (2.7)$$

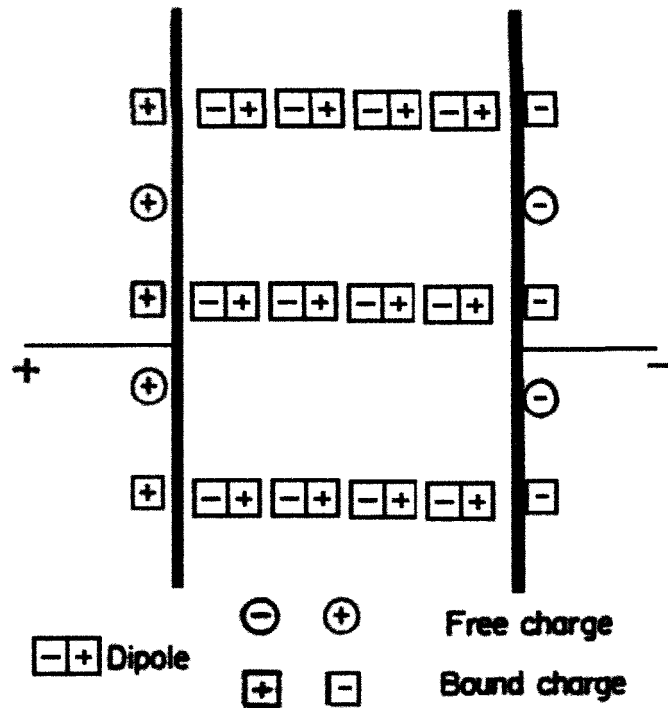


Fig. 2.1 Schematic representation of dielectric polarization [von Hippel, 1954]. (With permission of John Wiley & Sons, New York)

Polarization of a dielectric may be classified according to

1. **Electronic or Optical Polarization**
2. **Orientalional Polarization**
3. **Atomic or Ionic Polarization**
4. **Interfacial Polarization.**

We shall consider the first three of these in turn and the last mechanism will be treated in chapter 4.

2.2 ELECTRONIC POLARIZATION

The classical view of the structure of the atom is that the center of the atom consists of positively charged protons and electrically neutral neutrons. The electrons move about the nucleus in closed orbits. At any instant the electron and the nucleus form a dipole with a moment directed from the negative charge to the positive charge. However the axis of the dipole changes with the motion of the electron and the time average of the

dipole moment is zero. Further, the motion of the electron must give rise to electromagnetic radiation and electrical noise. The absence of such effects has led to the concept that the total electronic charge is distributed as a spherical cloud the center of which coincides with the nucleus, the charge density decreasing with increasing radius from the center.

When the atom is situated in an electric field the charged particles experience an electric force as a result of which the center of the negative charge cloud is displaced with respect to the nucleus. A dipole moment is induced in the atom and the atom is said to be **electronically polarized**.

The electronic polarizability α_e may be calculated by making an approximation that the charge is spread uniformly in a spherical volume of radius R . The problem is then identical with that in section 1.3. The dipole moment induced in the atom was shown to be

$$\mu_e = (4\pi \epsilon_0 R^3)E \quad (1.42)$$

For a given atom the quantity inside the brackets is a constant and therefore the dipole moment is proportional to the applied electric field. Of course the dipole moment is zero when the field is removed since the charge centers are restored to the undisturbed position.

The electronic polarizability of an atom is defined as the dipole moment induced per unit electric field strength and is a measure of the ease with which the charge centers may be dislocated. α_e has the dimension of $F m^2$. Dipole moments are expressed in units called **Debye** whose pioneering studies in this field have contributed so much for our present understanding of the behavior of dielectrics. 1 **Debye unit** = $3.33 \times 10^{-30} C m$.

α_e can be calculated to a first approximation from atomic constants. For example the radius of a hydrogen atom may be taken as 0.04 nm and α_e has a value of $10^{-41} F m^2$. For a field strength of 1 MV/m which is a high field strength, the displacement of the negative charge center, according to eq. (1.42) is $10^{-16} m$; when compared with the atomic radius the displacement is some 10^{-5} times smaller. This is due to the fact that the internal electric field within the atom is of the order of $10^{11} V/m$ which the external field is required to overcome.

Table 2.1
Electronic polarizability of atoms²

Element	radius (10^{-10} m)	α_e (10^{-40} F m ²)
He	0.93	0.23
Ne	1.12	0.45
Ar	1.54	1.84
Xe	1.9	4.53
I	1.33	6.0
Cs	3.9	66.7

(with permission of CRC Press).

Table 2.1 shows that the electronic polarizability of rare gases is small because their electronic structure is stable, completely filled with 2, 10, 18 and 36 electrons. As the radius of the atom increases in any group the electronic polarizability increases in accordance with eq. (1.42). Unlike the rare gases, the polarizability of alkali metals is more because the electrons in these elements are rather loosely bound to the nucleus and therefore they are displaced relatively easily under the same electric field. In general the polarizability of atoms increases as we move down any group of elements in the periodic table because then the atomic radius increases.

Fig. 2.2³ shows the electronic polarizability of atoms. The rare gas atoms have the lowest polarizability and Group I elements; alkali metals have the highest polarizability, due to the single electron in the outermost orbit. The intermediate elements fall within the two limits with regularity except for aluminum and silver.

The ions of atoms of the elements have the same polarizability as the atom that has the same number of electrons as the ion. Na^+ has a polarizability of 0.2×10^{-40} F m² which is of the same order of magnitude as α_e for Ne. K^+ is close to Argon and so on. The polarizability of the atoms is calculated assuming that the shape of the electron is spherical. In case the shape is not spherical then α_e becomes a tensor quantity; such refinement is not required in our treatment.

Molecules possess a higher α_e in view of the much larger electronic clouds that are more easily displaced. In considering the polarizability of molecules we should take into account the **bond polarizability** which changes according to the axis of symmetry. Table 2.2² gives the polarizabilities of molecules along three principal axes of symmetry in units of 10^{-40} Fm². The mean polarizability is defined as $\alpha_m = (\alpha_1 + \alpha_2 + \alpha_3)/3$. Table 2.3 gives the polarizabilities of chemical bonds parallel and normal to the bond axis and also

the mean value for all three directions in space, calculated according to $\alpha_m = (\alpha_{||} + 2\alpha_{\perp})/3$. The constant 2 appears in this equation because there are two mutually perpendicular axes to the bond axis.

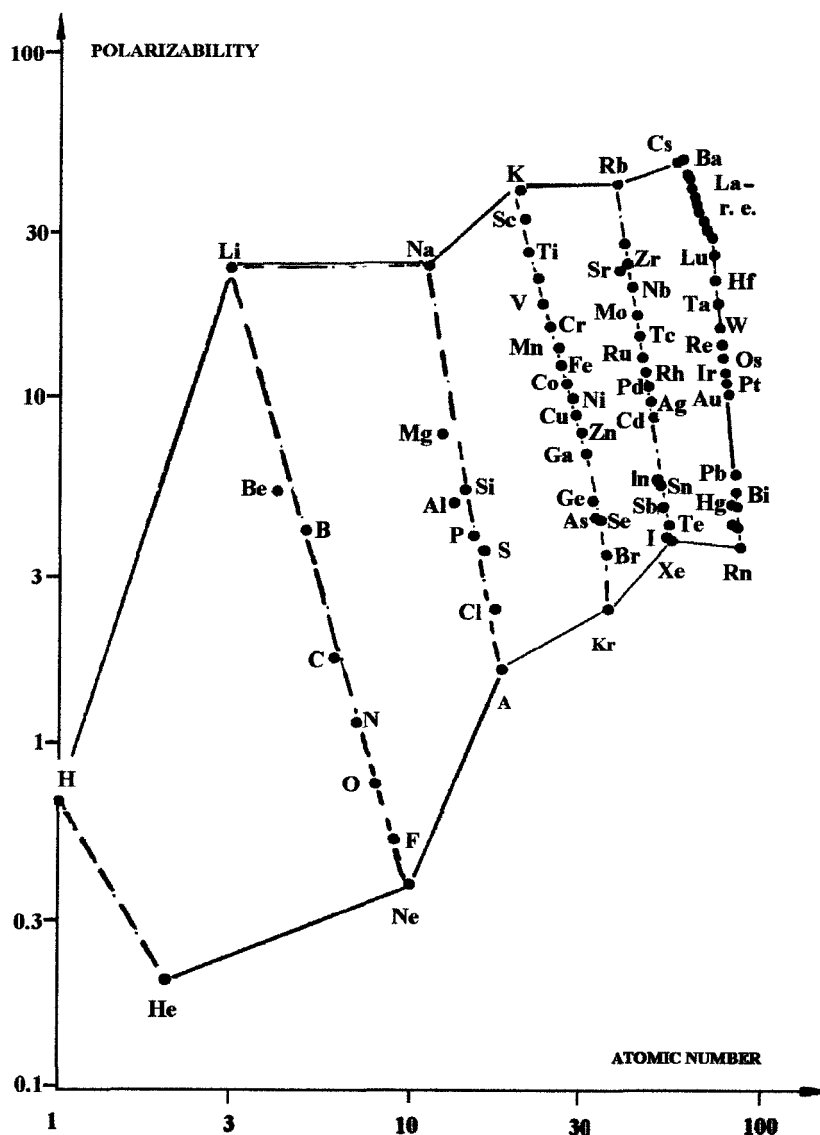


Fig. 2.2 Electronic polarizability (F/m^2) of the elements versus the atomic number. The values on the y axis must be multiplied by the constant $4\pi\epsilon_0 \times 10^{-30}$. (Jonscher, 1983: With permission of the Chelsea Dielectric Press, London).

It is easy to derive a relationship between the dielectric constant and the electronic polarizability. The dipole moment of an atom, by definition of α_e , is given by $\alpha_e E$ and if N is the number of atoms per unit volume then the dipole moment per unit volume is $N\alpha_e E$. We can therefore formulate the equation

$$\mathbf{P} = N\alpha_e \mathbf{E} \quad (2.8)$$

Substituting equation (2.5) on the left side and equation (1.22) on the right yields

$$\varepsilon = 4\pi NR^3 + 1 \quad (2.9)$$

This expression for the dielectric constant in terms of N and R is the starting point of the dielectric theory. We can consider a gas at a given pressure and calculate the dielectric constant using equation (2.9) and compare it with the measured value. For the same gas the atomic radius R remains independent of gas pressure and therefore the quantity $(\varepsilon-1)$ must vary linearly with N if the simple theory holds good for all pressures.

Table 2.4 gives measured data for hydrogen at various gas pressures at 99.93° C and compares with those calculated by using equation (2.9)⁴. At low gas pressures the agreement between the measured and calculated dielectric constants is quite good. However at pressures above 100 M pa (equivalent to 1000 atmospheric pressures) the calculated values are lower by more than 5%. The discrepancy is due to the fact that at such high pressures the intermolecular distance becomes comparable to the diameter of the molecule and we can no longer assume that the neighboring molecules do not influence the polarizability.

Table 2.2

Polarizability of molecules [3]

Molecule	α_1	α_2	α_3	α_m
H ₂	1.04	0.80	0.80	0.88
O ₂	2.57	1.34	1.34	5.25
N ₂ O	5.39	2.30	2.30	3.33
CCl ₄	11.66	11.66	11.66	11.66
HCl	3.47	2.65	2.65	2.90

(with permission from Chelsea dielectric press).

Table 2.3
Polarizability of molecular bonds [3]

Bond	$\alpha_{ }$	$\alpha_{\perp}$	α_m	comments
H-H	1.03	0.80	0.88	
N-H	0.64	0.93	0.83	NH ₃
C-H	0.88	0.64	0.72	aliphatic
C-Cl	4.07	2.31	2.90	
C-Br	5.59	3.20	4.0	
C-C	2.09	0.02	0.71	aliphatic
C-C	2.50	0.53	1.19	aromatic
C=C	3.17	1.18	1.84	
C=O	2.22	0.83	1.33	carbonyl

(with permission from Chelsea dielectric press).

The increase in the electric field experienced by a molecule due to the polarization of the surrounding molecules is called the **internal field**, E_i . When the internal field is taken into account the induced dipole moment due to electronic polarizability is modified as

$$\mu_e = \alpha_e E_i \quad (2.10)$$

The internal field is calculated as shown in the following section.

2.3 THE INTERNAL FIELD

To calculate the internal field we imagine a small spherical cavity at the point where the internal field is required. The result we obtain varies according to the shape of the cavity; Spherical shape is the least difficult to analyze. The radius of the cavity is large enough in comparison with the atomic dimensions and yet small in comparison with the dimensions of the dielectric.

Let us assume that the net charge on the walls of the cavity is zero and there are no short range interactions between the molecules in the cavity. The internal field, E_i at the center of the cavity is the sum of the contributions due to

1. The electric field due to the charges on the electrodes (free charges), E_1 .
2. The field due to the bound charges, E_2 .
3. The field due to the charges on the inner walls of the spherical cavity, E_3 . We may also view that E_3 is due to the ends of dipoles that terminate on the surface of the sphere. We have shown in chapter 1 that the polarization of a dielectric P gives rise to a surface

charge density. Note the direction of P_n which is due to the negative charge on the cavity wall.

4. The field due to the atoms within the cavity, E_4 .

Table 2.4

Measured and calculated dielectric constant [4]. $R=91 \times 10^{-12}$ m

pressure (MPa)	density Kg/m^3	N $(\text{m}^3) \times 10^{26}$	ϵ equation (2.9)	ϵ (measured)
1.37	0.439	2.86	1.00266	1.00271
4.71	1.482	9.82	1.00898	1.00933
8.92	2.751	18.62	1.01670	1.01769
14.35	4.305	29.91	1.02628	1.02841
22.43	6.484	46.80	1.03966	1.04446
48.50	12.496	101.21	1.07750	1.09615
93.81	20.374	195.78	1.12840	1.18599
124.52	24.504	259.86	1.15620	1.24687
144.39	26.833	301.32	1.17232	1.28625

We can express the internal field as the sum of its components:

$$\mathbf{E}_i = \mathbf{E}_1 + \mathbf{E}_2 + \mathbf{E}_3 + \mathbf{E}_4 \quad (2.11)$$

The sum of the field intensity $\mathbf{E}_1$ and $\mathbf{E}_2$ is equal to the external field,

$$\mathbf{E} = \mathbf{E}_1 + \mathbf{E}_2 \quad (2.12)$$

$\mathbf{E}_3$ may be calculated by considering a small element of area dA on the surface of the cavity (Fig. 2.3). Let θ be the angle between the direction of $\mathbf{E}$ and the charge density $\mathbf{P}_n$. $\mathbf{P}_n$ is the component of $\mathbf{P}$ normal to the surface, i.e.,

$$\mathbf{P}_n = \mathbf{P} \cos \theta \quad (2.13)$$

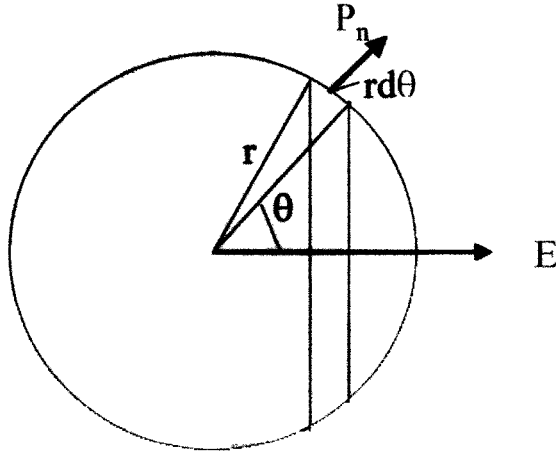


Fig. 2.3 Calculation of the internal field in a dielectric.

The charge on dA is

$$dq = P \cos \theta dA \quad (2.14)$$

The electric field at the center of the cavity due to charge dq is

$$d\mathbf{E}_3' = \frac{P \cos \theta dA}{4\pi\epsilon_0 r^2} \quad (2.15)$$

We are interested in finding the field which is parallel to the applied field. The component of $d\mathbf{E}_3'$ along $\mathbf{E}$ is

$$\begin{aligned} d\mathbf{E}_3 &= d\mathbf{E}_3' \cos \theta \\ &= \frac{P \cos^2 \theta dA}{4\pi\epsilon_0 r^2} \end{aligned} \quad (2.16)$$

All surface elements making an angle θ with the direction of $\mathbf{E}$ give rise to the same $d\mathbf{E}_3$. The area dA is equal to

$$\begin{aligned} dA &= 2\pi r \sin \theta \cdot r d\theta \\ &= 2\pi r^2 \sin \theta d\theta \end{aligned} \quad (2.17)$$

The total area so situated is the area of the annular ring having a radii of r and $r + d\theta$. i.e., Substituting equation (2.16) in (2.17) gives

$$d\mathbf{E}_3 = \frac{\mathbf{P} \cos^2 \theta}{4\pi\epsilon_0 r^2} \cdot 2\pi r^2 \sin \theta d\theta \quad (2.18)$$

Because of symmetry the components perpendicular to $\mathbf{E}$ cancel out. We therefore get

$$\mathbf{E}_3 = \int_0^\pi \frac{\mathbf{P} \cos^2 \theta}{2\epsilon_0} \sin \theta d\theta \quad (2.19)$$

$$= \frac{\mathbf{P}}{3\epsilon_0} \quad (2.20)$$

The charge on the element considered also gives rise to an electric field in a direction perpendicular to $\mathbf{E}$ and this component is

$$dE'_3 \sin \theta = \frac{\mathbf{P} \cos \theta \sin \theta dA}{4\pi\epsilon_0 r^2}$$

Substituting expression (2.17) in this expression and integrating we get

$$\int_0^\pi \frac{\mathbf{P} \cos \theta \sin^2 \theta d\theta}{2} = 0$$

Hence we consider only the parallel component of dE'_3 in calculating the electric field according to equation (2.16).

Because of symmetry the short range forces due to the dipole moments inside the cavity become zero, $\mathbf{E}_4 = 0$, for cubic crystals and isotropic materials. Substituting equation (2.20) in (2.11) we get

$$\mathbf{E}_i = \mathbf{E} + \frac{\mathbf{P}}{3\epsilon_0} \quad (2.21)$$

$\mathbf{E}_i$ is known as the **Lorentz field**. Substituting equation (2.5) in (2.21) we get

$$\mathbf{E}_i = \mathbf{E} \left(\frac{2 + \varepsilon}{3} \right) \quad (2.22)$$

Since

$$\mathbf{P} = \mathbf{E} \varepsilon_0 (\varepsilon - 1) = N \alpha_e \mathbf{E}_i$$

we get, after some simple algebra

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N \alpha_e}{3 \varepsilon_0} = \frac{N_A \alpha_e}{3 \varepsilon_0 V} \quad (2.23)$$

where V is the molar volume, given by M/ρ . By definition N is the number of molecules per unit volume. If ρ is the density (kg/m^3), M the molecular weight of dielectric (kg/mole), and N_A the Avagadro number, then

$$N_A = \frac{N \times M}{\rho} = N \times V \quad (2.24)$$

Substituting equation (2.24) in equation (2.23) we get,

$$\frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = \frac{N_A \alpha_e}{3 \varepsilon_0} = R \quad (2.25)$$

in which R is called the **molar polarizability**. Equation (2.25) is known as the Clausius-Mosotti equation. The left side of equation (2.25) is often referred to as C-M factor. In this equation all quantities except α_e may be measured and therefore the latter may be calculated.

Maxwell deduced the relation that $\varepsilon = n^2$ where n is the refractive index of the material. Substituting this relation in equation (2.25), and ignoring for the time being the restriction that applies to the Maxwell equation, the discussion of which we shall postpone for the time being, we get

$$\frac{n^2 - 1}{n^2 + 2} \frac{M}{\rho} = \frac{N_A \alpha_e}{3 \varepsilon_0} \quad (2.26)$$

Combining equations (2.25) and (2.26) we get

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{n^2 - 1}{n^2 + 2} \quad (2.27)$$

Equation (2.27) is known as the **Lorentz-Lorenz** equation. It can be simplified further depending upon particular parameters of the dielectric under consideration. For example, gases at low pressures have $\varepsilon \approx 1$ and equation (2.23) simplifies to

$$\varepsilon = 1 + \frac{N\alpha_e}{\varepsilon_0} \quad (2.28)$$

If the medium is a mixture of several gases then

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \sum_{j=1}^{J=k} \frac{N_j \alpha_{ej}}{3\varepsilon_0} \quad (2.29)$$

where N_j and α_{ej} are the number and electronic polarizability of each constituent gas.

Equation (2.23) is applicable for small densities only, because of the assumptions made in the derivation of Clausius-Mosotti equation. The equation shows that the factor $(\varepsilon - 1) / (\varepsilon + 2)$ increases with N linearly assuming that α_e remains constant. This means that ε should increase with N faster than linearly and there is a critical density at which ε should theoretically become infinity. Such a critical density is not observed experimentally for gases and liquids.

It is interesting to calculate the displacement of the electron cloud in practical dielectrics. As an example, Carbon tetrachloride (CCl_4) has a dielectric constant of 2.24 at 20°C and has a density of 1600 kg/m^3 . The molecular weight is $156 \times 10^{-3} \text{ Kg/mole}$. The number of molecules per m^3 is given by equation (2.24) as:

$$\begin{aligned} N &= N_A \frac{\rho}{M} = 6.03 \times 10^{23} \times \frac{1600}{156 \times 10^{-3}} \\ &= 6.2 \times 10^{27} \text{ m}^{-3} \end{aligned}$$

Let us assume an electric field of 1MV/m which is relatively a high field strength. Since $P = N\mu = E \epsilon_0 (\epsilon_r - 1)$ the induced dipole moment is equal to

$$\mu = \frac{10^6 \times 8.854 \times 10^{-12} \times 1.24}{6.2 \times 10^{27}} = 1.78 \times 10^{-33} \text{ C m}$$

CCl₄ has 74 electrons. Hence each electron-proton pair, on the average has a dipole moment of $(1.78 \times 10^{-32}) / 74 = 2.4 \times 10^{-35} \text{ Cm}$. The average displacement of the electron cloud is obtained by dividing the dipole moment by the electronic charge, $1.5 \times 10^{-16} \text{ m}$. This is roughly 10^{-6} times that of the molecular size.

Returning to equation (2.25) a rearrangement gives

$$\epsilon = \frac{1 + 2\rho R / M}{1 - \rho R / M} \quad (2.30)$$

where the molar polarizability R refers to the compound. Denoting the molar polarizability and atomic weight of individual atoms as r and m respectively we can put $R = \sum r$ and $M = \sum m$. Table 2.5 shows the application of equation (2.30) to an organic molecule.

As an example we consider the molecule of heptanol: Formula CH₃ (CH₂)₅ (CH₂OH), $\rho = 824 \text{ kg/m}^3$ (20°C), b. p. = 176° C, m. p. = -34.1° C.

$$\alpha_T = \sum \alpha = (7 \times 1.06 + 16 \times 0.484 + 1 \times 0.67) \times 10^{-40} = 15.83 \times 10^{-40} \text{ F/m}^2$$

$$M = \sum m = 7 \times 12.01 + 16 \times 1.01 + 1 \times 16.00 = 116.23$$

$$N_A \alpha_T \rho / 3 \epsilon_0 M = 0.2556, \epsilon = 2.03, \text{ Measured } n^2 = (1.45)^2 = 2.10$$

Equation (2.25) is accurate to about 1% when applied to non-polar polymers. Fig. 2.4⁵ shows the variation of the dielectric constant with density in non-polar polymers and the relation that holds may be expressed as

$$\frac{1}{\rho} \left(\frac{\epsilon - 1}{\epsilon + 2} \right) \cong 0.325 \quad (2.31)$$

The Clausius-Mosotti function is linearly dependent on the density.

Table 2.5
Calculation of molar polarizability of a compound⁶

Atom structure	$\alpha (x 10^{-40} \text{ F m}^2)$	m
C	1.064	12.01
H	0.484	1.01
O (alcohol)	0.671	16.00
O(carbonyl)	0.973	-
O(ether)	0.723	-
O(ester)	0.722	-
Si	4.17	28.08
F (one/carbon)	0.418	19.00
Cl	2.625	35.45
Br	3.901	79.91
I	6.116	126.90
S	3.476	32.06
N	1.1-1.94	14.01
Structural effects		
Double bond	1.733	
Triple bond	2.398	
3-member ring	0.71	
4-member ring	0.48	

(with permission from North Holland Co.).

2.4 ORIENTATIONAL POLARIZATION

The Clausius-Mosotti equation is derived assuming that the relative displacement of electrons and nucleus is elastic, i.e., the dipole moment is zero after the applied voltage is removed. However molecules of a large number of substances possess a dipole moment even in the absence of an electric field. In the derivation of equation (2.23) the temperature variation was not considered, implying that polarization is independent of temperature. However the dielectric constant of many dielectrics depends on the temperature, even allowing for change of state. The theory for calculating the dielectric constant of materials possessing a permanent dipole moment is given by Debye.

Dielectrics, the molecules of which possess a permanent dipole moment, are known as polar materials as opposed to non-polar substances, the molecules of which do not possess a permanent dipole moment. Di-atomic molecules like H_2 , N_2 , Cl_2 , with homopolar bonds do not possess a permanent dipole moment. The majority of molecules

that are formed out of dissimilar elements are polar; the electrons in the valence shell tend to acquire or lose some of the electronic charge in the process of formation of the molecule. Consequently the center of gravity of the electronic charge is displaced with respect to the positive charges and a permanent dipole moment arises.

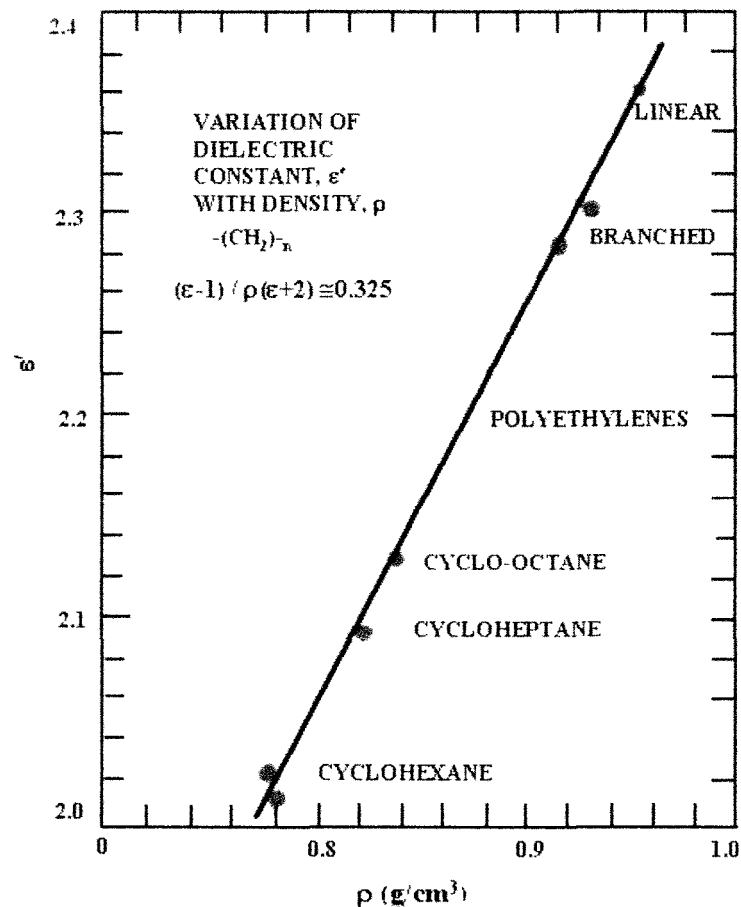


Fig. 2.4 Linear variation of dielectric constant with density in non-polar polymers [Link, 1972]. (With permission from North Holland Publishing Co.)

For example, in the elements of HCl, the outer shell of a chlorine atom has seven electrons and hydrogen has one. The chlorine atom, on account of its high electronegativity, appropriates some of the electronic charge from the hydrogen atom with the result that the chlorine atom becomes negatively charged and the hydrogen atom is depleted by the same amount of electronic charge. This induces a dipole moment in the molecule directed from the chlorine atom to the hydrogen atom. The distance between the atoms of hydrogen and chlorine is 1.28×10^{-10} m and it possesses a dipole moment of 1.08 D.

Since the orientation of molecules in space is completely arbitrary, the substance will not exhibit any polarization in the absence of an external field. Due to the fact that the electric

field tends to orient the molecule and thermal agitation is opposed to orientation, not all molecules will be oriented. There will be a preferential orientation, however, in the direction of the electric field. Increased temperature, which opposes the alignment, is therefore expected to decrease the orientational polarization. Experimentally this fact has been confirmed for many polar substances.

If the molecule is symmetrical it will be non-polar. For example a molecule of CO_2 has two atoms of oxygen distributed evenly on either side of a carbon atom and therefore the CO_2 molecule has no permanent dipole moment. Carbon monoxide, however, has a dipole moment. Water molecule has a permanent dipole moment because the O-H bonds make an angle of 105° with each other.

Hydrocarbons are either non-polar or possess a very small dipole moment. But substitution of hydrogen atoms by another element changes the molecule into polar. For example, Benzene (C_6H_6) is non-polar, but monochlorobenzene ($\text{C}_6\text{H}_5\text{Cl}$), nitrobenzene ($\text{C}_6\text{H}_5\text{NO}_2$), and monoiodobenzene ($\text{C}_6\text{H}_5\text{I}$) are all polar. Similarly by replacing a hydrogen atom with a halogen, a non-polar hydrocarbon may be transformed into a polar substance. For example methane (CH_4) is non-polar, but chloroform (CHCl_3) is polar.

2.5 DEBYE EQUATIONS

We have already mentioned that the polarization of the dielectric is zero in the absence of an electric field, even for polar materials, because the orientation of molecules is random with all directions in space having equal probability. When an external field is applied the number of dipoles confined to a solid angle $d\Omega$ that is formed between θ and $\theta + d\theta$ is given by the Boltzmann distribution law:

$$n(\theta) = A \exp\left(-\frac{v}{kT}\right) d\Omega \quad (2.32)$$

in which v is the potential energy of the dipole and $d\Omega$ is the solid angle subtended at the center corresponding to the angle θ , where k , is the Boltzmann constant, T the absolute temperature and A is a constant that depends on the total number of dipoles. Consider the surface area between the angles θ and $\theta + d\theta$ on a sphere of radius r (fig. 2.5),

$$\begin{aligned} ds &= 2\pi r \sin \theta \cdot r d\theta \\ &= 2\pi r^2 \sin \theta d\theta \end{aligned} \quad (2.33)$$

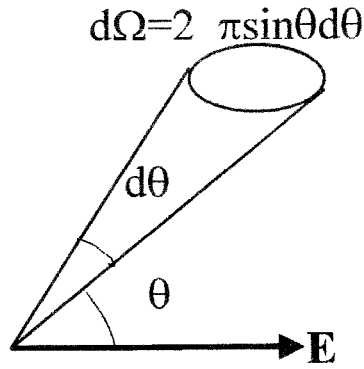


Fig. 2.5 Derivation of the Debye equation. The solid angle is $d\Omega$.

Since the solid angle is defined as ds/r^2 the solid angle between θ and $\theta + d\theta$ is

$$d\Omega = 2\pi \sin \theta d\theta \quad (2.34)$$

We recall that the total solid angle subtended at the center of the sphere is 4π steradians.

This may be checked by the formula,

$$d\Omega = \int_0^\pi 2\pi \sin \theta d\theta = 4\pi$$

The potential energy of a dipole in an electric field is

$$v = -\mu E \quad (2.35)$$

Since the dipoles in the solid angle are situated at an angle of θ the potential energy is reduced to

$$v = -\mu E \cos \theta \quad (2.36)$$

Substituting equations (2.33) and (2.34) in (2.32) we get

$$n(\theta) = A \exp\left(\frac{\mu E \cos \theta}{kT}\right) 2\pi \sin \theta d\theta \quad (2.37)$$

Since a dipole of permanent moment μ making an angle θ with the direction of the electric field contributes a moment $\mu \cos \theta$, the contribution of all dipoles in $d\Omega$ is equal to

$$\mu(\theta) = n(\theta) \mu \cos \theta \quad (2.38)$$

Therefore the average moment per dipole in the direction of the electric field is given by the ratio of the dipole moment due to all molecules divided by the number of dipoles,

$$\mu_o = \frac{\int_0^\pi n(\theta) \mu \cos \theta d\theta}{\int_0^\pi n(\theta) d\theta} \quad (2.39)$$

Note that the average dipole moment cannot be calculated by dividing equation (2.38) by (2.37), because we must consider all values of θ from 0 to π before averaging. Substituting equations (2.37) and (2.38) in (2.39) we get

$$\mu_o = \frac{\int_0^\pi A \exp\left(\frac{\mu E \cos \theta}{kT}\right) (2\pi \sin \theta) \mu \cos \theta d\theta}{\int_0^\pi A \exp\left(\frac{\mu E \cos \theta}{kT}\right) 2\pi \sin \theta d\theta} \quad (2.40)$$

To avoid long expressions we make the substitution

$$\frac{\mu E}{kT} = x \quad (2.41)$$

and

$$\cos \theta = y \quad (2.42)$$

The substitution simplifies equation (2.40) to

$$\frac{\mu_0}{\mu} = \frac{\int_{-1}^1 y \exp(xy) dy}{\int_{-1}^1 \exp(xy) dy} \quad (2.43)$$

Recalling that

$$\int \exp(xy) dy = \frac{\exp(xy)}{x}$$

$$\int y \exp(xy) dy = \frac{e^{xy}}{x^2} (xy - 1)$$

equation (2.43) reduces to

$$\frac{\mu_0}{\mu} = \frac{(e^x + e^{-x})}{(e^x - e^{-x})} - \frac{1}{x} \quad (2.44)$$

Since the first term on the right side of equation (2.44) is equal to $\coth x$ we get

$$\frac{\mu_0}{\mu} = \coth x - \frac{1}{x} = L(x) \quad (2.45)$$

$L(x)$ is called the **Langevin function** and it was first derived by Langevin in calculating the mean magnetic moment of molecules having permanent magnetism, where similar considerations apply.

The Langevin function is plotted in Fig. 2.6. For small values of x , i.e., for low field intensities, the average moment in the direction of the field is proportional to the electric field. This can be proved by the following considerations:

Substituting the identities for the exponential function in equation (2.44) we have

$$e^x = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \dots$$

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \dots \quad (2.46)$$

$$L(x) = \coth x - \frac{1}{x} = \frac{1}{x} \left(\frac{x^2}{3} - \frac{x^4}{45} + \dots \right) \quad (2.47)$$

For small values of x higher powers of x may be neglected and the Langevin function may be approximated to

$$L(x) = \frac{1}{3}x \cong \frac{\mu E}{3kT} \quad (2.48)$$

For large values of x however, i.e., for high electric fields or low temperatures, $L(x)$ has a maximum value of 1, though such high electric fields or low temperatures are not practicable as the following example shows.

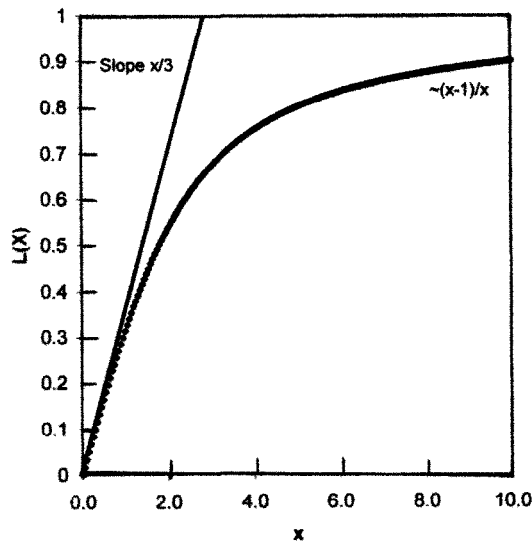


Fig. 2.6 Langevin function with x defined according to eq. (2.41). For small values of x , $L(x)$ is approximately equal to $x/3$.

Let us consider the polarizability of HCl in an electric field of 150 kV/m. The dipole moment of HCl molecule is $1D=3.3 \times 10^{-30}$ C m so that, at room temperature

$$x = \frac{\mu E}{kT} = \frac{3.3 \times 10^{-30} \times 150 \times 10^3}{1.38 \times 10^{-23} \times 293} = 1.25 \times 10^{-4}$$

Note that x is a dimensionless quantity. The Langevin function for this small value of x , because of approximation (2.48) is

$$L(x) = \frac{x}{3} = 4 \times 10^{-5}$$

The physical significance of this parameter is that, on the average we can say that 0.004% of molecules are oriented in the direction of the applied field. At higher electric fields or lower temperatures $L(x)$ will be larger. Increase of electric field, of course, is equivalent to applying higher torque to the dipoles. Decrease of temperature reduces the agitation velocity of molecules and therefore rotating them on their axis is easier. An example is that it is easier to make soldiers who are standing in attention obey a command than people in a shopping mall. Table 2.6 gives $L(x)$ for select values of x .

The field strength required to increase the $L(x)$ to, say 0.2, may be calculated with the help of equation (2.48). Substituting the appropriate values we obtain $E = 7 \times 10^8 \text{ V/m}$, which is very high indeed. Clearly such high fields cannot be applied to the material without causing electrical breakdown. Hence for all practical purposes equation (2.48) should suffice.

Table 2.6

Langevin Function for select values of x

x	$\coth x$	$L(x)$
10^{-4}	10^4	0
0.01	100.003	0.0033
0.1	10.033	0.0333
0.15	6.716	0.0499
0.18	5.615	0.0598
0.21	4.83	0.0698

Since $L(x)$ was defined as the ratio of μ_0 / μ in equation (2.45) we can express equation (2.48) as

$$\mu_0 = \frac{\mu^2 E}{3kT} \quad (2.49)$$

Therefore the polarizability due to orientational polarization is

$$\alpha_0 = \frac{\mu_0}{E} = \frac{\mu^2}{3kT} \quad (2.50)$$

The meanings associated with μ_0 and μ should not create confusion. The former is the average contribution of a molecule to the polarization of the dielectric; the latter is its inherent dipole moment due to the molecular structure. A real life analogy is that μ represents the entire wealth of a rich person whereas μ_0 represents the donation the person makes to a particular charity. The latter can never exceed the former; in fact the ratio $\mu_0 / \mu \ll 1$ in practice as already explained.

The dipole moment of many molecules lies, in the range of 0.1-3 Debye units and substituting this value in equation (2.48) gives a value $\alpha_0 \approx 10^{-40} \text{ F m}^2$, which is the same order of magnitude as the electronic polarizability. The significance of equation (2.49) is that although the permanent dipole moment of a polar molecule is some 10^6 times larger than the induced dipole moment due to electronic polarization of non-polar molecules, the contribution of the permanent dipole moment to the polarization of the material is of the same order of magnitude, though always higher (i.e., $\alpha_0 > \alpha_e$). This is due to the fact that the measurement of dielectric constant involves weak fields.

The polarization of the dielectric is given by

$$\mathbf{P} = N\alpha_0 \mathbf{E} = \frac{N\mu^2 \mathbf{E}}{3kT} \quad (2.51)$$

If the dielectric is a mixture of several components then the dielectric constant is given by

$$\mathbf{P} = \frac{\mathbf{E}}{3kT} \sum_{j=1}^{j=n} N_j \mu_j^2 \quad (2.52)$$

where N_j and μ_j are the number and dipole moment of constituent materials respectively. In the above equation $\mathbf{E}$ should be replaced by $\mathbf{E}_i$, equation (2.22) if we wish to include the influence of the neighboring molecules.

2.6 EXPERIMENTAL VERIFICATION OF DEBYE EQUATION

In deriving the **Debye equation** (2.51) the dipole moment due to the electronic polarizability was not taken into consideration. The electric field induces polarization P_e and this should be added to the polarization due to orientation. The total polarization of a polar dielectric is therefore

$$\mathbf{P} = NE(\alpha_e + \frac{\mu^2}{3kT}) \quad (2.53)$$

Equation (2.25) now becomes

$$R = \frac{\varepsilon - 1}{\varepsilon + 2} \frac{M}{\rho} = \frac{N_A}{3\varepsilon_0} \left(\alpha_e + \frac{\mu^2}{3kT} \right) \quad (2.54)$$

For mixtures of polar materials the Debye equation becomes

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{1}{3\varepsilon_0} \sum_{j=1}^{j=k} N_j \left(\alpha_{ej} + \frac{\mu_j^2}{3kT} \right) \quad (2.55)$$

According to equation (2.54) a plot of R as a function of $1/T$ yields a straight line with an intercept

$$\frac{N_A \alpha_e}{3\varepsilon_0} \quad \text{and a slope} \quad \frac{N_A \mu^2}{9k\varepsilon_0} \quad (2.56)$$

Fig. 2.7 shows results of measurements of C-M factor as a function of $1/T$ for silicone fluids⁷. Silicone fluid, also known as poly(dimethyl siloxane) has the formula $(\text{CH}_3)_3\text{Si} - [\text{OSi}(\text{CH}_3)_2]_x \text{OSi}(\text{CH}_3)_3$. It has a molecular weight $(162.2 + 72.2 x)$ g /mole, $x = 1$ to

1000 and an average density of 960 kg/m^3 . The advantage of using silicone fluid is that liquids of various viscosities with the same molecular weight can be used to examine the influence of temperature on the dielectric constant. The polarizabilities calculated from the intercept is 1.6×10^{-37} , 2.9×10^{-37} , and $3.7 \times 10^{-37} \text{ Fm}^2$ for 200, 500 and 1000 cSt viscosity. These are the sum of the electronic and atomic polarizabilities. The calculated α_e using data from Table 5 for a monomer ($x = 1$, No. of atoms: C – 8, H – 24, Si – 3, O – 2) is $3.4 \times 10^{-39} \text{ F m}^2$. For an average value of $x = 100$ (for transformer grade $x = 40$) electronic polarizability alone has a value of the same order mentioned above and the liquid is therefore slightly polar.

The slopes give a Dipole moment of 5.14, 8.3 and 9.4 D respectively. Sutton and Mark⁸ give a dipole moment of 8.47 D for 300 cSt fluid which is in reasonable agreement with the value for 200 cSt. Application of Onsagers theory (see section 2.8) to these liquids gives a value for the dipole moment of 8.62, 12.1 and 13.1 D respectively. To obtain agreement of the dipole moment obtained from fig. 2.7 and theory, a correlation factor of $g = 2.8$, 2.1 and 2.1 are employed, respectively.

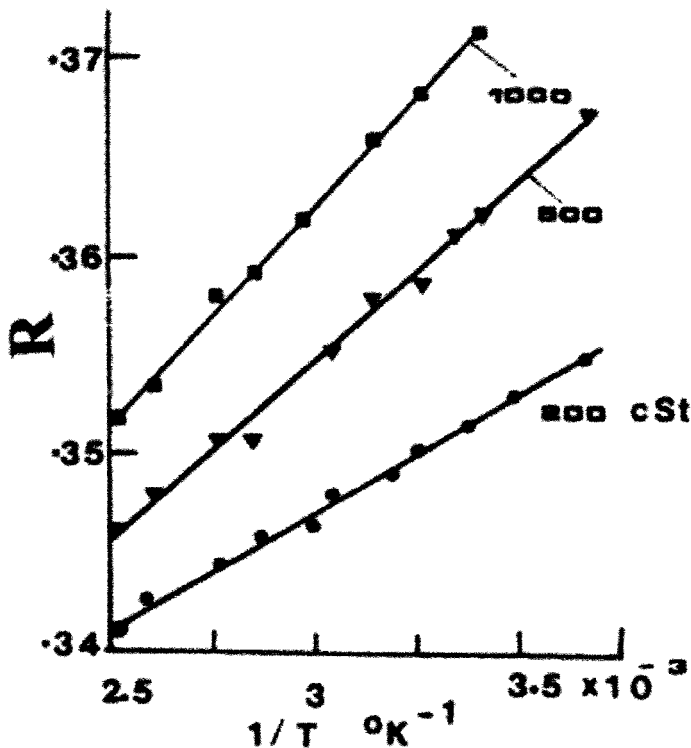


Fig. 2.7 Molar polarizability in silicone fluids versus temperature for various viscosities (Raju, ©1988, IEEE.).

Fig. 2.8 shows the calculated R - T variation for some organic liquids using the data shown in Table 2.7. From plots similar to fig. 2.8 we can separate the electronic polarizability and the permanent dipole moment. For non-polar molecules the slope is zero because, $\mu = 0$.

The Debye equation is valid for high density gases and weak solutions of polar substances in non-polar solvents. However the dipole moments calculated from ϵ for the gas (vapor) phase differ appreciably from the dipole moments calculated using measurements of ϵ of the liquid phase. As an example the data for CHCl_3 (Chloroform) are given in Table 2.8. The dielectric constant of the vapor at 1 atmospheric pressure at 100°C is 1.0042. In the gaseous phase it has a dipole moment of 1.0 D. In the liquid phase, at 20°C , $N = 7.47 \times 10^{27} \text{ m}^{-3}$ and equation (2.54) gives a value of 1.6 D.

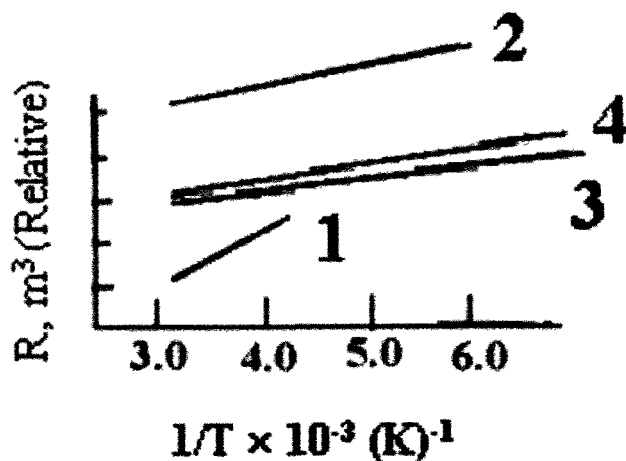


Fig. 2.8 Molar polarizability versus temperature for several polar molecules. The dipole moment may be calculated from the slope. 1-water (H_2O), 2-Methyl alcohol (CH_4O), 3-Ethyl alcohol ($\text{C}_2\text{H}_6\text{OH}$), 4-Propanol ($\text{C}_3\text{H}_8\text{O}$).

Table 2.7
Dielectric properties of selected liquids

Name	Formula	$M (\times 10^{-3} \text{ kg/mole})$	$\rho \text{ Kg/m}^3$	ϵ	$\mu \text{ (Gas Phase) D}$	n	ϵ_∞
Water	H_2O	18	1000	80.4	1.85	1.33	3.48
Nitrobenzene	$\text{C}_6\text{H}_5\text{NO}_2$	123.1	1210	35.7	4.1	1.55	
Methanol	CH_4O	32.04	791.4	33.62	1.70	1.33	1.33
Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	112.56	1105.8	5.62	1.7	1.52	
Chloroform	CHCl_3	119.38	1483.2	4.81	1.0	1.44	
Ethyl alcohol	$\text{C}_2\text{H}_6\text{OH}$	46.07	789.3	24.35	1.69	1.36	1.36
1-propanol	$\text{C}_3\text{H}_8\text{O}$	60.11	803.5	20.44	1.68	1.45	1.45

1 D = $3.3 \times 10^{-30} \text{ Cm}$

2.7 SPONTANEOUS POLARIZATION

Neglecting electronic polarization we can write equation (2.54) as

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N\mu^2}{9\varepsilon_0 kT} \quad (2.57)$$

For a given material at a given temperature, the right side of equation (2.57) is a constant and we can make a substitution

$$\frac{N\mu^2}{9\varepsilon_0 k} = T_c \quad (2.58)$$

The constant T_c is called the **critical temperature** and has the dimension of K. Equation (2.57) then simplifies to

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{T_c}{T} \quad (2.59)$$

For values of $T \leq T_c$ equation (2.59) can be satisfied only if ε becomes infinitely large. The physical significance is that the material possesses a very large value of ε at temperatures lower than a certain critical temperature. The material is said to be spontaneously polarized at or below T_c , and above T_c it behaves as a normal dielectric. A similar behavior obtains in the theory of magnetism. Below a certain temperature, called the **Curie Temperature**, the material becomes spontaneously magnetized and such a material is called ferromagnetic. In analogy, dielectrics that exhibit spontaneous polarization are called ferroelectrics.

The slope of the ε - T plots ($d\varepsilon /dT$) changes sign at the Curie temperature as data for several ferroelectrics clearly show. Certain polymers such as poly(vinyl chloride) also exhibit a change of slope in $d\varepsilon /dT$ as T is increased⁹ and the interpretation of this data in terms of the Curie temperature is deferred till ch. 5.

Table 2.8Dielectric constant of Chloroform and Water²

T (° C)	ϵ (CHCl ₃)	T (° C)	ϵ (H ₂ O)	ρ for H ₂ O (kg/m ³)
180	2.92	75	-	974.89
140	3.32	60	66.8	983.24
100	3.72	50	69.9	988.07
20	4.81	40	73.3	992.24
-20	5.61	30	76.6	995.67
-40	6.12	20	80.3	998.23
-60	6.76	10	84.0	999.73
		0 (liquid)	88.1	998.97

We may obtain an idea of magnitude for the critical temperature for polar dielectrics with the help of equation (2.58). Water is a polar dielectric and a molecule has a permanent dipole moment of 6.23×10^{-30} C m (1.87 D). The number of molecules is given by equation (2.24) as

$$N = \frac{6.03 \times 10^{23} \times 10^3}{18 \times 10^{-3}} = 3.35 \times 10^{28} m^{-3}$$

Substituting these values in equation (2.58) we get $T_c \approx 930^\circ$ C. Apparently, water at room temperature should be ferroelectric according to Debye theory, but this is not so. Hence an improvement to the theory has been suggested by Onsager which is dealt with in the next section.

Ferroelectric materials with high permittivity are used extensively in microwave devices, high speed microelectronics, radar and communication systems. Ceramic barium titanate (BaTiO₃) exhibits high permittivity, values ranging from 2000-10,000, depending upon the method of preparation, grain size, etc¹⁰. Bismuth titanate ceramics (Bi₂Ti₂O₇) exhibit even larger permittivity near the Curie temperature. Fig. 2.9¹¹ shows the measured permittivity at various temperatures and frequencies. If we ignore the frequency dependence for the time being, as this will be discussed in chapters 3 and 4, the permittivity remains relatively constant up to $\sim 200^\circ$ C and increases fast beyond 300-400°C. Permittivity as high as 50,000 is observed at the Curie temperature of $\sim 700^\circ$ C. Table 2.9 lists some well known ferro-electric crystals.

2.8 ONSAGER'S THEORY

As mentioned before, the Debye theory is satisfactory for gases, vapors of polar liquids and dilute solutions of polar substances in non-polar solvents. For pure polar liquids the value of μ calculated from equation (2.54) does not agree with the dipole moments calculated from measurements on the vapor phase where the Debye equation is known to apply, as Table 2.7 shows. Further, the prediction of the Curie point below where the liquid is supposed to be spontaneously polarized, does not hold true except in some special cases.

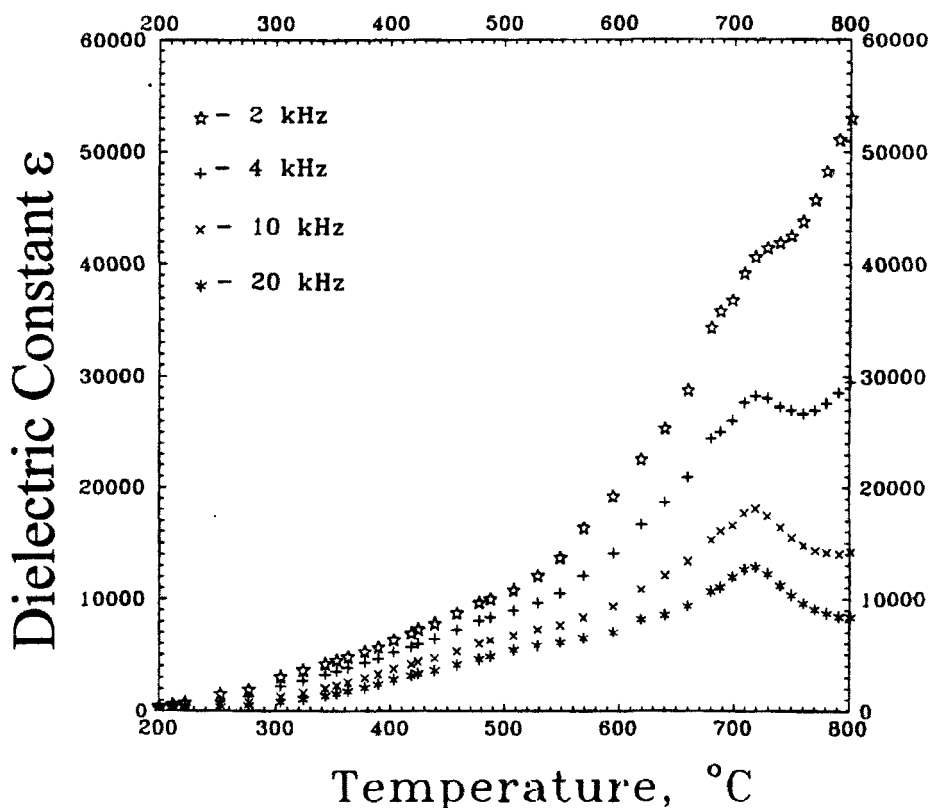


Fig. 2.9 Dielectric constant ϵ of Bismuth titanate ceramic which is ferro-electric as a function of temperature. The dependence of ϵ on frequency is discussed in chapter 3. (Yardonov et. al., 1998: With permission of J. Phys. D.: Appl. Phys.).

Onsager¹² attributed these difficulties to the inaccuracy caused by neglecting the reaction field which was introduced in chapter 1. The field which acts upon a molecule in a polarized dielectric may be decomposed into a cavity field and a reaction field which is proportional to the total electric moment and depends on the instantaneous orientation of the molecule. The mean orientation of a molecule is determined by the orienting force

couple exerted by the cavity field upon the electric moment of the molecule. The approach of Debye, though a major step in the development of dielectric theory, is equivalent to the assumption that the effective orienting field equals the average cavity field plus the reaction field. This is inaccurate because the reaction field does not exert a torque on the molecule. The Onsager field is therefore lower than that considered by Debye by an amount equal to the reaction field.

Onsager considered a spherical cavity of the dimension of a molecule with a permanent dipole moment μ at its center. It is assumed that the molecule occupies a sphere of radius r , i.e., $\frac{4}{3}\pi r^3 N = 1$ and its polarizability is isotropic. The field acting on a molecule is made up of three components:

- (1) The externally applied field $\mathbf{E}$ along Z direction.
- (2) A field due to the polarization of the dielectric.
- (3) A reaction field $\mathbf{R}$ due to the dipole moment μ of the molecule itself.

The three components combined together give rise to the **Lorentz field** E_i which was shown to be

$$\mathbf{E}_i = \mathbf{E} \left(\frac{2 + \epsilon}{3} \right) \quad (2.22)$$

The reaction field of a dipole in the center of a dielectric sphere is given by (1.70)

$$\mathbf{R} = \frac{2(\epsilon_1 - \epsilon_2)}{4\pi\epsilon_0\epsilon_2 r^3 (2\epsilon_1 + \epsilon_2)} \mu \quad (1.70)$$

in which ϵ_1 and ϵ_2 are the dielectric constants of the medium outside and inside the sphere. For a cavity, $\epsilon_2 = 1$ and omitting the suffix for the other dielectric constant we obtain

$$\mathbf{R} = \frac{1}{4\pi\epsilon_0} \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \frac{\mu}{r^3} \quad (1.68)$$

All the quantities on the right side of this equation are constants and we can make the substitution

Table 2.9
Selected Ferro-electric Crystals

NAME	FORMULA	T _c (K)	P × 10 ⁻⁴ (μC/m ²) at	T (K)
Potassium dihydrogen phosphate	KH ₂ PO ₄	123	4.75	96
Potassium dideuterium phosphate	KD ₂ PO ₄	213	4.83	180
Rubidium dihydrogen phosphate	RbH ₂ PO ₄	147	5.6	90
Rubidium dideuterium phosphate	RbD ₂ DO ₄	218	-	-
Barium titanate	BaTiO ₃	393	26.0	300
Lead titanate	PbTiO ₂	763	>50	300
Cadmium titanate	CdTiO ₂	55	-	-
Pottassium niobate	KnbO ₃	708	30.0	523
Rochelle salt	NaKC ₄ H ₄ O ₆ . 4D ₂ O	297 ^A 255	0.25	278
Deuterated Rochelle salt	NaKC ₄ H ₂ D ₂ O ₆ . 4D ₂ O	308 ^A 251	0.35	279

^A There are upper and lower T_c

Source: F. Jona and G. Shirane, Ferroelectric Crystals, Pergamon Press, NY, 1962, p. 389 (with permission).

$$\mathbf{R} = f\mu \quad (2.60)$$

in which

$$f = \frac{1}{4\pi\epsilon_0 r^3} \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \quad (2.61)$$

Equations (1.69) and (1.70) were derived assuming that the dipole was rigid, *i.e.*, its dipole moment was constant. This is only an approximation because the reaction field increases the dipole moment, the increase being $\alpha\mathbf{R}$. This in turn will increase the reaction field to $\mathbf{R}_m$ and equation (2.60) will be modified as

$$\mathbf{R}_m = f(\mu + \alpha\mathbf{R}_m) \quad (2.62)$$

in which α is the polarizability of the molecule. Therefore

$$\mathbf{R}_m = \frac{f}{1 - f\alpha} \mu \quad (2.63)$$

Substituting the value of f from equation (2.61) we can rewrite this equation as

$$\mathbf{R}_m = \frac{2(\varepsilon - 1)}{4\pi\varepsilon_0 r^3 (2\varepsilon + 1) - 2\alpha(\varepsilon - 1)} \mu \quad (2.64)$$

We can now use Equation (2.26) to substitute for α ,

$$\alpha = \frac{3\varepsilon_0}{N} \frac{n^2 - 1}{n^2 + 2} \quad (2.26)$$

We further note that

$$\frac{4}{3} \pi N r^3 = 1 \quad (2.65)$$

Substituting equations (2.26) and (2.65) in (2.64) we get

$$\mathbf{R}_m = \frac{2N(\varepsilon - 1)(n^2 + 2)}{9\varepsilon_0(n^2 + 2\varepsilon)} \mu \quad (2.66)$$

Similarly we can deduce the modified dipole moment from equation

$$\mu_m = \mu + \alpha \mathbf{R}_m \quad (2.67)$$

Combining equations (2.67) and (2.63) we get

$$\mu_m = \frac{\mu}{1 - f\alpha} \quad (2.68)$$

Substituting for f from equation (2.61) and for r from equation (2.65) we get

$$\mu_m = \frac{2\varepsilon + 1}{3(2\varepsilon + n^2)}(n^2 + 2)\mu \quad (2.69)$$

Kirkwood¹³ gives an alternate expression for the modified dipole moment μ_m on the assumption that the total moment of the molecule consists of a point dipole at the center of a sphere of radius a of dielectric constant unity, as opposed to n^2 implied in equation (2.69),

$$\frac{\mu_m}{\mu} = \frac{1}{\left[1 - \frac{2(\varepsilon - 1)}{(2\varepsilon + 1)} \frac{\alpha N}{3\varepsilon_0}\right]}$$

Substituting equation (2.26) in this equation yields

$$\frac{\mu_m}{\mu} = \frac{1}{1 - \left[\frac{2(\varepsilon - 1)}{(2\varepsilon + 1)} \right] \left[\frac{n^2 - 1}{n^2 + 2} \right]} \quad (2.70)$$

At the beginning of this section it was mentioned that a part of the internal field is due to the reaction field $\mathbf{R}$. When the dipole is directed by an external field, the average value of the reaction field in the direction of $\mathbf{E}$ is $\mathbf{R}_m \langle \cos \theta \rangle$ where the symbols enclosing $\cos \theta$ signifies average value, assuming that the reaction field follows the direction of μ instantaneously. Since $\mathbf{R}_m$ has the same direction as μ at any instant, $\mathbf{R}_m \cos \theta$ does not contribute to the directing torque. We have to, therefore, apply a correction to the internal field as

$$E = E_i - R_m \langle \cos \theta \rangle \quad (2.71)$$

The average value of $\cos \theta$ is given by the expression (2.39) as

$$\langle \cos \theta \rangle = \frac{\mu_0}{\mu} = \frac{\int_0^\pi n(\theta) \cos \theta d\theta}{\int_0^\pi n(\theta) d\theta} \quad (2.39)$$

$$= \frac{\mu E}{3kT} \quad (2.72)$$

Substituting equation (2.71) in (2.72) we get

$$\langle \cos \theta \rangle = \frac{\mu}{3kT} (E_i - R_m \langle \cos \theta \rangle) \quad (2.73)$$

Rearrangement gives

$$\langle \cos \theta \rangle = \frac{\mu}{\mu R_m + 3kT} E_i \quad (2.74)$$

Equation (2.54) now becomes

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N}{3\varepsilon_0} \left(\alpha + \frac{\mu^2}{3kT + \mu R_m} \right) \quad (2.75)$$

Substituting for R_m from equation (2.66) we get

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{N}{3\varepsilon_0} \left(\alpha_e + \frac{\mu^2}{3kT + \frac{2N\mu^2}{9\varepsilon_0} \frac{(\varepsilon - 1)(n^2 + 2)}{(n^2 + 2\varepsilon)}} \right) \quad (2.76)$$

Because of equation (2.26) the above equation may be rewritten as

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} - \frac{(n^2 - 1)}{(n^2 + 2)} = \frac{N}{3\varepsilon_0} \left(\frac{\mu^2}{3kT + \frac{2N\mu^2}{9\varepsilon_0} \frac{(\varepsilon - 1)(n^2 + 2)}{(n^2 + 2\varepsilon)}} \right) \quad (2.77)$$

After lengthy algebra to obtain the relation between ε and μ Onsager derives the expression

$$\frac{N\mu^2}{9\varepsilon_0 kT} = \frac{(\varepsilon - n^2)(2\varepsilon + n^2)}{(n^2 + 2)^2} \quad (2.78)$$

leading to

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} - \frac{(n^2 - 1)}{(n^2 + 2)} = \frac{N\mu^2}{3\varepsilon_0 kT} \frac{\varepsilon(n^2 + 2)}{(2\varepsilon + n^2)(\varepsilon + 2)} \quad (2.79)$$

We note here that the left side of equation (2.79) is not zero because, the relationship, $\varepsilon = n^2$ does not hold true for polar substances at steady fields.

We may approximate equation (2.79) with regard to specific conditions as follows:

(1) For non-polar materials $\mu = 0$. We then obtain

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)} = \frac{(n^2 - 1)}{(n^2 + 2)} \quad (2.27)$$

which is the Lorenz-Lorentz equation.

(2) For polar gases at low pressures the following approximations apply:

$$\varepsilon \approx 1, (\varepsilon - 1) \ll 1, (n^2 - 1) \ll 1, (n^2 + 1) \approx 3 \text{ and}$$

equation (2.79) simplifies to

$$(\varepsilon - 1) = \frac{N\mu^2}{3\varepsilon_0 kT} \quad (2.57)$$

which is the Debye equation for polar gases.

If we view the Onsager's equation (2.79) as a correction to the Debye equation then it is of interest to calculate the magnitude of the modified reaction field $\mathbf{R}_m$ and the modified dipole moment μ_m from equations (2.66) and (2.69). Table 2.8 gives the appropriate data and the calculated values. $\mathbf{R}_m$ has a magnitude of the order of 10^9 V/ m. To obtain the significance of this field we compare the electric field that exists due to the dipole along its axis and along the perpendicular to the axis. Eq. (1.26) gives the potential due to a dipole at a point with co-ordinates (ϕ, θ) as

$$\phi(r, \theta) = \frac{1}{4\pi\varepsilon_0} \frac{\mu \cos \theta}{r^2} \quad (1.26)$$

The field due to the dipole has two components given by

$$E_r = -\frac{d\phi}{dr} a_r \quad (2.80)$$

$$E_\theta = -\frac{1}{r} \frac{d\phi}{d\theta} a_\theta \quad (2.81)$$

The field on the axis of a dipole is therefore

$$E_{(r,0)} = \frac{\mu}{2\pi\epsilon_o r^3} \quad (2.82)$$

The field perpendicular to the axis is

$$E_{(r,\pi/2)} = \frac{\mu}{4\pi\epsilon_o r^3} \quad (2.83)$$

For a dipole of moment 1D the two fields at a distance of $r = 50$ nm are $E_{(r,0)} = 500$ MV/m and $E_{(r,\pi/2)} = 250$ MV/m. Comparing these values with R_m we find that the latter is 10 - 20 times larger, making a significant difference to the calculation of the dipole moment. For the effective increase in the dipole moment, the ratio μ_m/μ is between 25-50%.

The Onsager's equation (2.78) may be used to determine whether a polar monomer contributes all of its dipole moment to the polarization of the polymer. This will be true if the dipole moment of the polymer is higher than that of the monomer. The monomer of poly(vinyl acetate) (PVAc) is polar, the measured dielectric constant at 55°C is 9.5¹⁴, $\epsilon_\infty = n^2 = 2$, mol. wt. = 86 g/mole. In the case of a polymer equation, (2.78) may be rewritten as:

$$\mu^2 = \frac{9\epsilon_0 kT(\epsilon_s - \epsilon_\infty)(2\epsilon_s + \epsilon_\infty)M_w}{N_A \rho \epsilon_s (\epsilon_\infty + 2)^2} \quad (2.84)$$

in which N_A is the avagadro number, M_w is the molecular wt. of the monomer, and ρ the density of the polymer. Collecting the values, $\epsilon_s = 9.5$, $\epsilon_\infty = 2$, $T = 328$ K, $k = 1.38 \times 10^{-23}$ J/K, $\rho = 1100$ Kg/m³, $N_A = 6.03 \times 10^{23}$, eq. (2.77) gives $\mu = 2.1$ D. Since the monomer has a dipole moment of 1.79 D the monomer contributes 100% to the polarization. Another example of the application of Onsager's equation is given in Ch. 5.

2.9 THEORY OF KIRKWOOD

Kirkwood¹⁵ has developed a theory for the polarization of a non-polar dielectric in a homogenous electric field from a statistical point of view. We have already discussed the relation of the dielectric constant to the structural properties of the constituent molecules; this relation depends upon the internal field which is different from the externally applied field.

The internal field was calculated assuming that the contribution to the field of the molecules within the cavity was zero, i.e., $E_4 = 0$. Lorentz showed that this was true for cubic crystals and remarked that E_4 also becomes zero in a fluid for a random distribution of other molecules around the central one. These conclusions are equivalent to assuming that the electric moment of the molecule retains its average value, that is that the dipole remains rigid, through the various phases of thermal fluctuation.

Kirkwood suggests that the fluctuations in the induced dipole moments of a molecule require a correction to the Lorentz field, equation (2.22) and the formulas derived from it change appropriately. The approach is statistical and the dielectric is treated from the outset as a system of molecules rather than a continuum, thus eliminating the 'artificial' approach of a cavity.

In this approach the effects arising from inhomogeneity of the local field in the region occupied by the molecule is neglected. Further the dipole moment of a molecule is the product of its polarizability (α_T) in vacuum and the average field acting upon it. This field is partly due to the charges on the electrodes and partly due to other molecules surrounding it.

Kirkwood's theory considers an assembly of N spherically symmetrical particles placed in an electric field. At any instant a set of N vector equations gives the dipole moments of all the particles. These N vectorial equations are expressed as $3N$ scalar equations provided the co-ordinates of the points are known at that instant. In this model the polarizability is assumed to be at the center of the spherical molecule.

The electric field at a radial distance r due to a point dipole of moment μ , according to equation (1.34) is

$$\mathbf{E} = \mathbf{T}\mu \quad (1.14)$$

This field adds to the applied field and the dipole moment of the i^{th} molecule in an assembly changes to

$$\mu_i = \alpha E + \alpha \sum_{\substack{j=1 \\ j \neq i}}^N T_{ij} \mu_j \quad (2.85)$$

Since α has a magnitude comparable to the molecular volume and T_{ij} varies as $1/r^3$ (equation 1.14) we can expand the summation term as a power series with the expectation that it converges fast.

The internal field is obtained as a series:

$$(E_i)_{kirkwood} = [1 + (1 + \frac{\alpha}{4a^3})H + (\frac{1}{16} + \frac{3\alpha}{2a^3})H^2 + \dots] E \quad (2.86)$$

A comparison of equation (2.86) with equation (2.23) shows the Kirkwood theory is a correction that is applied to the internal field. A simplified version assumes that a geometrical correlation factor g may be used as a correction to the Onsager's equation.

If we consider only the first term on the right side of equation (2.86) then we get the expression

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N\alpha}{3\varepsilon_0} \quad (2.23)$$

which is the Clausius-Mossotti equation¹⁶. The first correction to the Clausius-Mosotti equation is suggested by Brown¹⁷ on the concept that the C-M parameter may be expressed as a polynomial of ρ rather than a linear function as implied by equation (2.25),

$$y = \frac{A_0}{\rho} + A_1 + A_2\rho + \dots \quad (2.87)$$

where

$$y = \frac{\varepsilon + 2}{\varepsilon - 1}$$

$$A_0 = \frac{3\varepsilon_0}{\alpha_e} \frac{M}{N_A} \quad (2.88)$$

and, A_1 and A_2 are constants that depend on the parameter $\alpha/\varepsilon_0 a^3$ where a is the molecular diameter.

An alternate form for ε is given by Bottcher as:

$$\varepsilon = 1 + 3\left(\frac{N\alpha}{3\varepsilon_0}\right) + 3\left(1 + \frac{\alpha}{4\pi a^3}\right)\left(\frac{N\alpha}{3\varepsilon_0}\right)^2 + 3\left(\frac{1}{16} + \frac{3\alpha}{2a^3}\right)\left(\frac{N\alpha}{3\varepsilon_0}\right)^3 + \dots \quad (2.89)$$

Returning to the Brown version of Kirkwood theory, equation (2.87), we first note that the left side is expressed as the inverse of the same part in the Clausius-Mossotti equation. The ratio

$$\frac{(\varepsilon - 1)}{(\varepsilon + 2)\rho}$$

should be constant for a given substance according to equation (2.25). If the measured and calculated dielectric constants differ to an unacceptable extent the Brown expression given by (2.87) should be tested.

To test this equation Brown¹⁸ assumed that molecules were spherically symmetrical in their mechanical and electrical properties and interact electrostatically as point dipoles. These assumptions are reasonably appropriate even if the molecules have a shape that departs from spherical symmetry appreciably, if the polarizability is considered as averages over all orientations. For molecules which are close together the neglect of quadruple and higher moments introduces additional errors.

Brown further noted that for highly asymmetric molecules averaging the properties of two molecules individually before they are allowed to interact, rather than of the properties of the interacting pair, is not quite accurate. The same reasoning applies to interacting clusters of higher magnitude. Moreover, one has to take into account the fact that electrostatic interactions are far from being of a dipole-dipole nature, that it is not even permissible to regard the molecule as equivalent to a dipole and a quadruple. For long chain molecules, as in polymers, these considerations are particularly important.

Notwithstanding these difficulties which are common to several theories, Brown presented a numerical analysis of equation (2.87) and compared it with more specialized formulas. He concluded that Bottcher's formula, equation (2.89), has no special advantage over the general formula, equation (2.87). To detect deviations of the behavior of molecules from the behavior predicted for spherical molecules we need to have a detailed knowledge of the radial distribution function of molecules¹⁹ and more precise data on dielectric constants.

A summary of the relevant formulas are given below.

(1) Clausius-Mosotti equation

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{N\alpha_e}{3\varepsilon_0} \quad (2.23)$$

(2) The empirical formula of Eykman²⁰

$$\frac{\varepsilon - 1}{\varepsilon^{1/2} + 0.4} = \frac{1}{1.4} \frac{N\alpha_e}{3\varepsilon_0} \quad (2.90)$$

(3) Bottcher Formula:

$$\varepsilon = 1 + 3\left(\frac{N\alpha}{3\varepsilon_0}\right) + 3\left(1 + \frac{\alpha}{4\pi a^3}\right)\left(\frac{N\alpha}{3\varepsilon_0}\right)^2 + 3\left(\frac{1}{16} + \frac{3\alpha}{2a^3}\right)\left(\frac{N\alpha}{3\varepsilon_0}\right)^3 + \dots \quad (2.89)$$

(4) Kirkwood's Formula: This version is given by Brown [17]

$$\frac{\varepsilon + 2}{\varepsilon - 1} = \frac{3\varepsilon_0}{N\alpha} - \frac{\alpha}{2\pi\varepsilon_0 a^3} + \frac{15N\alpha}{48\varepsilon_0} \quad (2.91)$$

(5) Brown formula :

$$y = \frac{A_0}{\rho} + A_1 + A_2\rho \quad (2.87)$$

Brown applied his equation to carbon disulphide (CS₂) and CO₂ at various densities and made a comparison with other formulas^{17, 18}. Here we show how to apply these formulas for one value of the gas density.

The data required for the application of equation (2.87) to CS₂ are:

Mol. Wt. = 76.13, M.P. = - 110.8° C, B. P. = 46.3° C, $\alpha_e = 9.622 \times 10^{-40}$ F m², $\rho = 1247$ kg/m³, ϵ (measured) = 2.624. The calculated values of ϵ according to different equations are shown in Table 2.10.

A second example of application of the equations to gases is with regard to ethylene (C₂H₄)²¹. As stated earlier the Clausius-Mosotti parameter

$$\frac{\epsilon - 1}{(\epsilon + 2)\rho} = \frac{N_A \alpha_e}{3M\epsilon_0} \quad (2.92)$$

should be a constant. Also, for gases with non-polar molecules the C-M parameter should be independent of temperature. To verify these conclusions the dielectric constant of ethylene was measured up to 500 atmospheres at temperatures of 25°C and 50°C. The measured dielectric constants are shown in fig. 2-10 along with density data for all gas pressures. The measured dielectric constant at 25°C at a gas pressure of 21.696 atmospheres is 1.0332. The density is 28.78 kg/m³ and $\alpha_e = 4.593 \times 10^{-40}$ Fm². Substituting these values the measured C-M parameter is equal to

$$\frac{(1.0332 - 1)}{(1.0332 + 2)28.78} = 3.8 \times 10^{-4} m^3 kg^{-1}$$

The calculated value from the right side of equation (2.92) is 3.71×10^{-4} kg/m³, which is within 2.4% of the measured value. However, the dielectric constant increases to 1.260 at a pressure of 66.9 atmospheres as expected by the theory (fig. 2.10), but the C-M parameter does not remain constant as shown in fig. 2.11.

The suggested reasons are (1) α_e may not remain constant and it may vary with density, (2) the Lorentz molecular model may not be applicable at high densities, requiring a modification of the equation.

Table 2.10
Calculated values of ϵ in CS₂

Equation	A ₀	A ₁	A ₂	ϵ	% difference
(2.23)	3550.57	-	-	2.668	1.68
(2.87)	3045.08	479.25	-96.362	2.628	0.152
(2.90)	3201.66			2.581	-1.639
(2.89)	4401.91			2.643	0.724
(2.91)	3782.88			2.637	0.495

W. F. Brown, J. Chem. Phys. 18, 1193, (1950)

Reverting to the formula of Kirkwood, the dielectric constant of a polar substance is expressed as²²

$$\epsilon = \epsilon_{\infty} + \frac{1}{9\epsilon_0} (n^2 + 2)^2 \left(\frac{\epsilon}{2\epsilon + n^2} \right) \left(\frac{N_A \mu^2}{kTV} \right) g \quad (2.93)$$

where μ is the dipole moment, n the refractive index, V , the molar volume (M/ρ in units of m³/kg) and g is called the correlation factor. This form of Kirkwood equation is easier to apply.

The correlation factor is a measure of local ordering in the dielectric²³. It has the value of unity if we imagine a molecule to be held fixed, and the average moment of a spherical region of finite radius within an infinite specimen is also the moment of the molecule. That is to say that when there is local ordering the net dipole moment in the spherical region surrounding the fixed molecule under consideration is zero. This means that fixing the position of a molecule does not influence the position of the surrounding molecules except the influence of the long range electrostatic forces.

On the other hand, if fixing the direction of one dipole tends to align the surrounding dipoles in a parallel direction the correlation factor is greater than one. Likewise, if fixing the direction of one dipole tends to align the surrounding dipoles in an anti-parallel direction the correlation factor is less than one. If the structure of the material is known it is possible to calculate g ; otherwise it becomes an empirical parameter which can be calculated by measuring ϵ and knowing μ .

The calculated values of g will give information about the structure of the material. For water Oster and Kirkwood²⁴ give a value of 2.65 assuming that $n = 1.33$. However the

calculated value of g depends strongly on the assumed value of n . For example, if we assume that $n = 4$ for water (as there is experimental evidence for this in the infrared region) we get $g = 1.09$. This value, close to unity, is interpreted as meaning that the structure of water molecule does not influence the orientational polarization. We also note that substitution of $g = 1$ in equation (2.93) results in an equation identical to that due to Onsager.

2.10 DIELECTRIC CONSTANT OF TWO MEDIA

We shall change our focus somewhat to the formulas that allow us to explain the dielectric constant of more than a single medium, on the basis of concepts that we have established so far. In engineering practice a mixture of several media is a common situation and different methods to calculate the dielectric constant are frequently used by practising engineers. As an example in power transformers cellulose materials are extensively used and then impregnated with transformer oil. Polymeric insulation in SF₆ insulated equipment is another example.

There are several different ways in which two different materials may occur in combination: Series, parallel, layered, impregnated, interspersed, etc. Some of these types are shown in fig. 2.12. A useful summary is provided by Morgan²⁵.

2.10.1 RALEIGH'S FORMULA

One of the earliest analysis of the dielectric constant of two component mixtures is due to Raleigh²⁶, who assumed that cylindrical particles of dielectric constant ϵ_p were mixed in a medium of the mixture is given as:

$$\frac{\epsilon - \epsilon_m}{\epsilon + \epsilon_m} = \frac{V_p(\epsilon_p - \epsilon_m)}{\epsilon_p + \epsilon_m} \quad (2.94)$$

where ϵ is the permittivity of the mixture and V_p is the volume fraction of the particles. The volume fraction of the medium before the mixture is prepared is V_m so that $V_p + V_m = 1$. The above equation may also be rewritten as:

$$\epsilon = \frac{\epsilon_m[x(\epsilon_p - \epsilon_m) + \epsilon_p + \epsilon_m]}{\epsilon_p + \epsilon_m - x(\epsilon_p - \epsilon_m)} \quad (2.95)$$

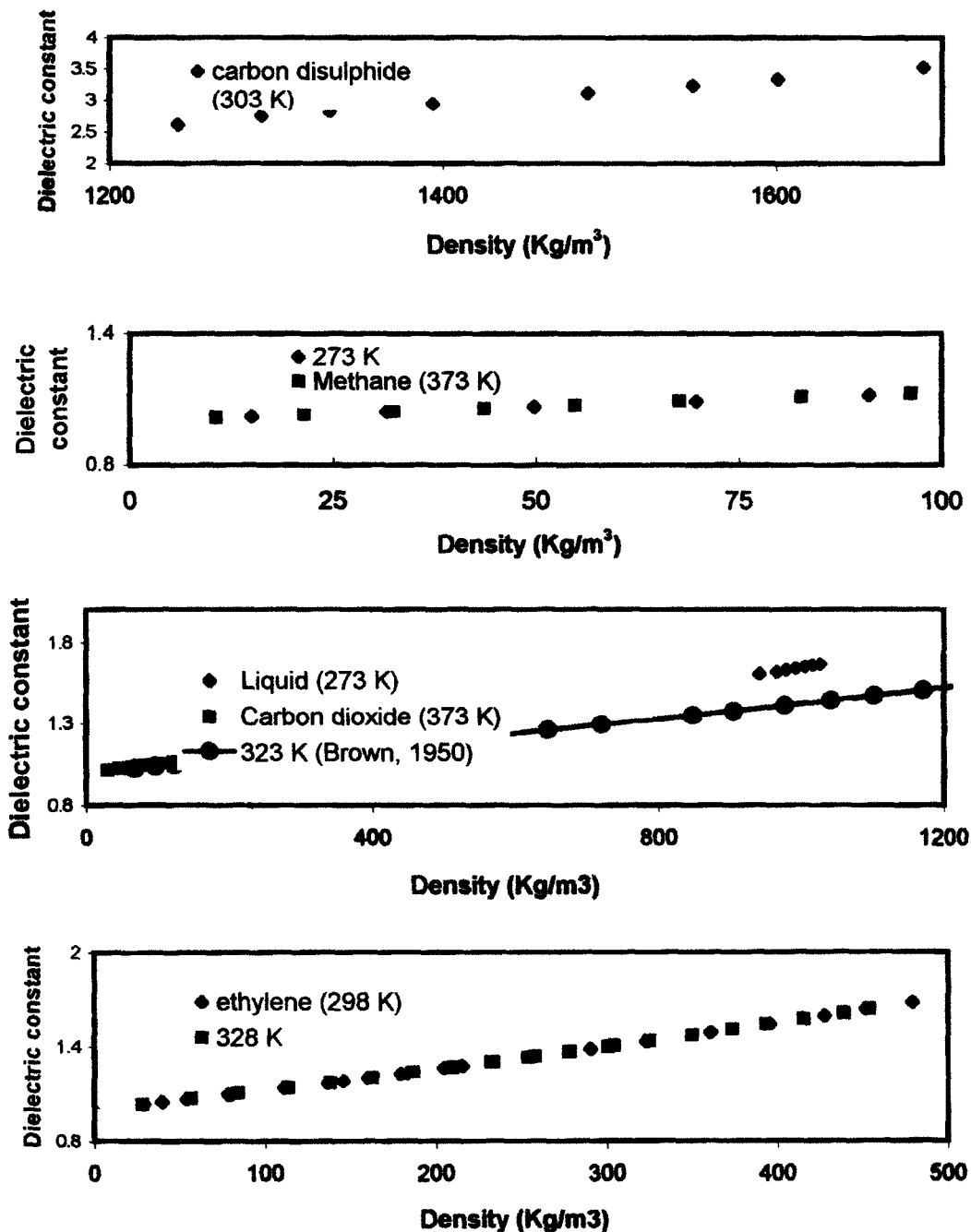


Fig. 2.10 Dielectric constant of non-polar materials versus density. Data are taken from: Methane & CO_2 (Cole, 1965; Gordon and Breach), Ethylene (David et. al. 1951, Gordon and Breach).

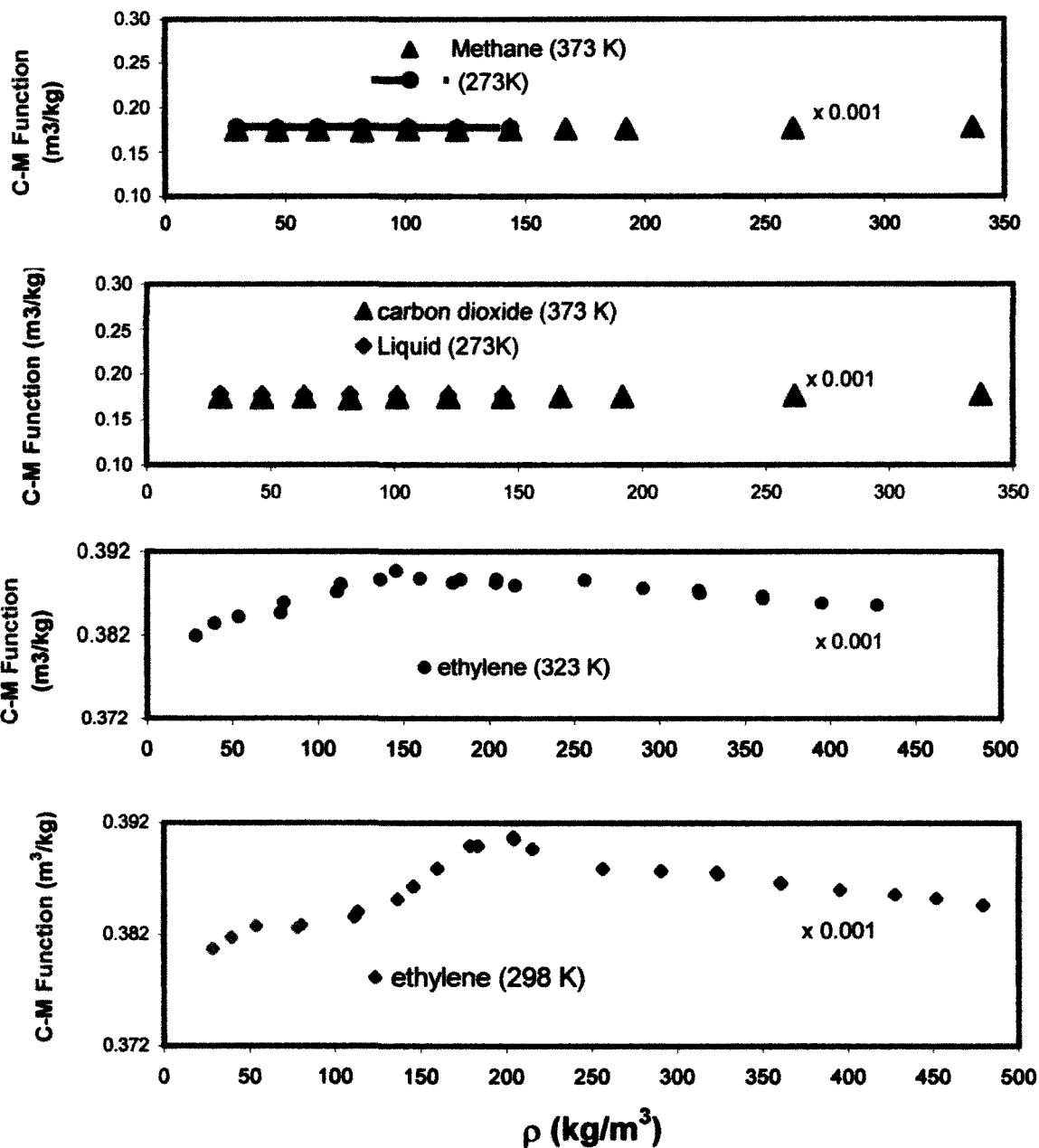


Fig. 2.11 C-M function versus density for non-polar substances. See legend for fig. 2.10 for source of data.

2.10.2 WIENER'S FORMULA

An alternative formulation is due to Wiener²⁷ who analyzed laminar mixtures and proposed the formula:

$$\frac{1}{\varepsilon + u} = \frac{V_p}{\varepsilon_p + u} + \frac{V_m}{\varepsilon_m + u}; \quad 0 \leq u \leq \infty \quad (2.96)$$

where u is a factor.

$$\frac{1}{\varepsilon} = \frac{V_p}{\varepsilon_p} + \frac{V_m}{\varepsilon_m} \quad (2.97)$$

For $u = \infty$ the equation for dielectrics in parallel is obtained.

$$\varepsilon = \varepsilon_p V_p + \varepsilon_m V_m \quad (2.98)$$

Bruggeman has suggested that for isotropic materials having randomly arranged grains the best approximation is $u = \sqrt[3]{\varepsilon_p \varepsilon_m}$.

2.10.3 FORMULA OF LICHTENECKER AND ROTHER

For powder and granular materials Lichtenecker and Rother suggested the formula

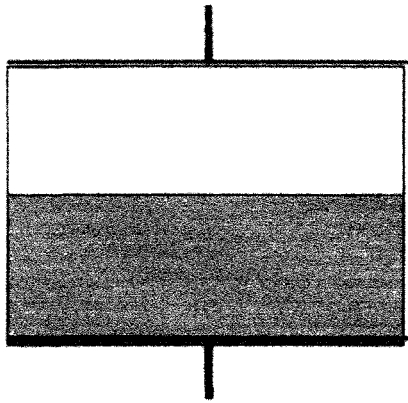
$$\varepsilon^k = V_p \varepsilon_p^k + V_m \varepsilon_m^k; \quad -1 \leq k \leq 1 \quad (2.99)$$

where k is a numerical variable.

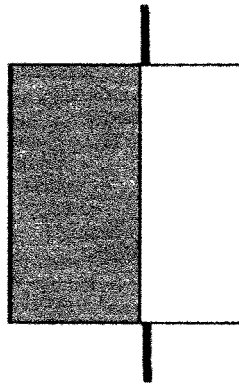
When $k = -1$ the formula for dielectrics in series, equation (2.97) is recovered. When $k = 1$ the formula for parallel dielectrics is obtained, equation (2.98). When $k = 0$ the exponential terms are expanded in an infinite series and neglecting the higher order terms one obtains:

$$\ln \varepsilon = V_p \ln \varepsilon_p + V_m \ln \varepsilon_m \quad (2.100)$$

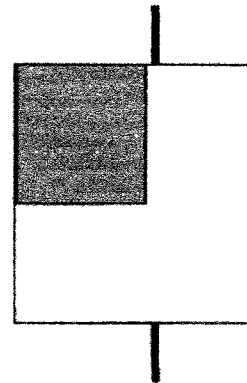
With $k = 0.5$ equation (2.99) reduces to the formula for refractive index upon substituting the Maxwell relation $\varepsilon = n^2$:



SERIES



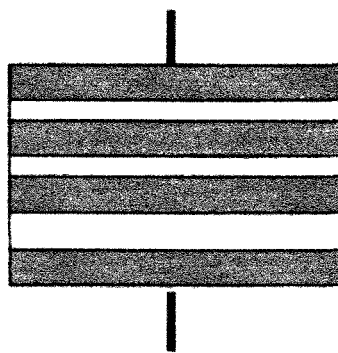
PARALLEL



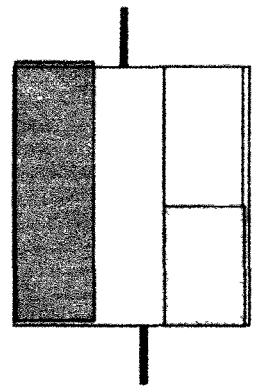
PILLAR



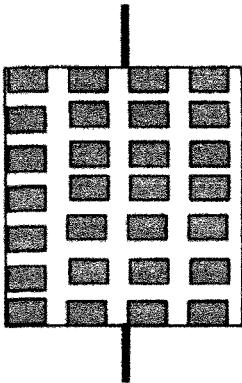
PARALLEL-LAYERED



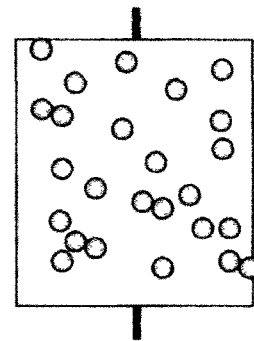
SERIES-LAYERED



SERIES-PARALLEL



UNIFORMLY DISPERSED



RANDOMLY DISPERSED

Fig. 2.12 Different arrangements for combination of two media.

For $k = 1/3$ the so called **Landau, Lifshits and Looyengas'** equation is obtained.

$$n = V_p n_p + V_m n_m \quad (2.101)$$

Lichtenecker's formula (2.99) may be generalized for any number of constituents as

$$\varepsilon^k = \sum_{j=1}^n f_j \varepsilon_j^k \quad (2.102)$$

where f_j is the relative volume fraction and ε_j the dielectric constant of the j^{th} constituent respectively, n the number of constituents and k is a constant between -1 and $+1$. Equation (2.102) is sometimes referred to as the series model and a geometric mean model for the dielectric constant of a mixture is given by²⁸

$$\varepsilon = \prod_{j=1}^n \varepsilon_j^{f_j} \quad (2.103)$$

Equations (2.102) and (2.103) have been used quite extensively in soil physics to correlate the measured electrical permittivity of a soil to its volumetric water content. A theoretical basis for the series model is provided by Zakri et. al.²⁸ who consider that the shapes of the inclusions (particles) is not uniform but follow a beta distribution. This approach is specific to geological mixtures or other mixtures where the particles have a distribution in shapes. In soils there are three constituents, solid, water and air, and using the subscripts s , w and a respectively, the series model gives the expression for the dielectric constant as

$$\varepsilon^k = (1-p)\varepsilon_s^k + (p-f_w)\varepsilon_a^k + f_w \varepsilon_w^k \quad (2.104)$$

where p is the porosity of the soil. Fig. 2.13 shows the calculated and measured dielectric constants along with the details of the characteristics of the soil samples according to Lichtenecker's formula. To appreciate the differences obtained with other formulas fig. 2.14 presents the values calculated for one sample and it can be seen that Lichtenecker's formula gives the best agreement.

2.10.4 Goldschmidt's Equation

For fibrous materials Goldschmidt²⁹ has proposed the equation:

$$\varepsilon = \frac{\varepsilon_m [\varepsilon_m + (\varepsilon_p - \varepsilon_m)(V_p + gV_m)]}{\varepsilon_m + gV_m(\varepsilon_p - \varepsilon_m)}; \quad 0 \leq g \leq 1 \quad (2.105)$$

where g is a constant that assumes different values for each assembly. Since $V_p + V_m = 1$ we can show that this equation reduces to the parallel case, equation (2.98) when $f = 0$.

The equation also reduces to the series equation (2.97) when $f = 1$. For cylindrical particles perpendicular to the electric field Goldschmidt found that $f = 0.5$ was satisfactory.

2.11 THE DISSIPATION FACTOR

Anticipating the discussion of alternating fields presented in chapter 3, the dissipation factor is defined as

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'} \quad (2.106)$$

The dissipation factor of a mixture of two dielectrics having dissipation factors $\tan \delta_p$ and $\tan \delta_m$ is given by:

$$\tan \delta = \frac{V_p \varepsilon'_m \tan \delta_p + V_m \varepsilon'_p \tan \delta_m (1 + \tan^2 \delta_p)}{V_p \varepsilon'_m + V_m \varepsilon'_p (1 + \tan^2 \delta_p)} \quad (2.107)$$

where the prime denotes the real part of the dielectric constant. The dissipation factor of dry dielectrics is usually small so that we can make the approximation $\tan^2 \delta \ll 1$ simplifying this equation into

$$\tan \delta = \frac{V_p \varepsilon'_m \tan \delta_p + V_m \varepsilon'_p \tan \delta_m}{V_p \varepsilon'_m + V_m \varepsilon'_p} \quad (2.108)$$

The dissipation factor measurements are usually carried out to determine the quality of the dielectric and adsorbed moisture is usually the second component. In such a situation

the second term in the numerator is usually small when compared with the first term and equation (2.108) may be approximated to:

$$\tan \delta = \frac{V_p \varepsilon'_m \tan \delta_p}{V_p \varepsilon'_m + V_m \varepsilon'_p} \quad (2.109)$$

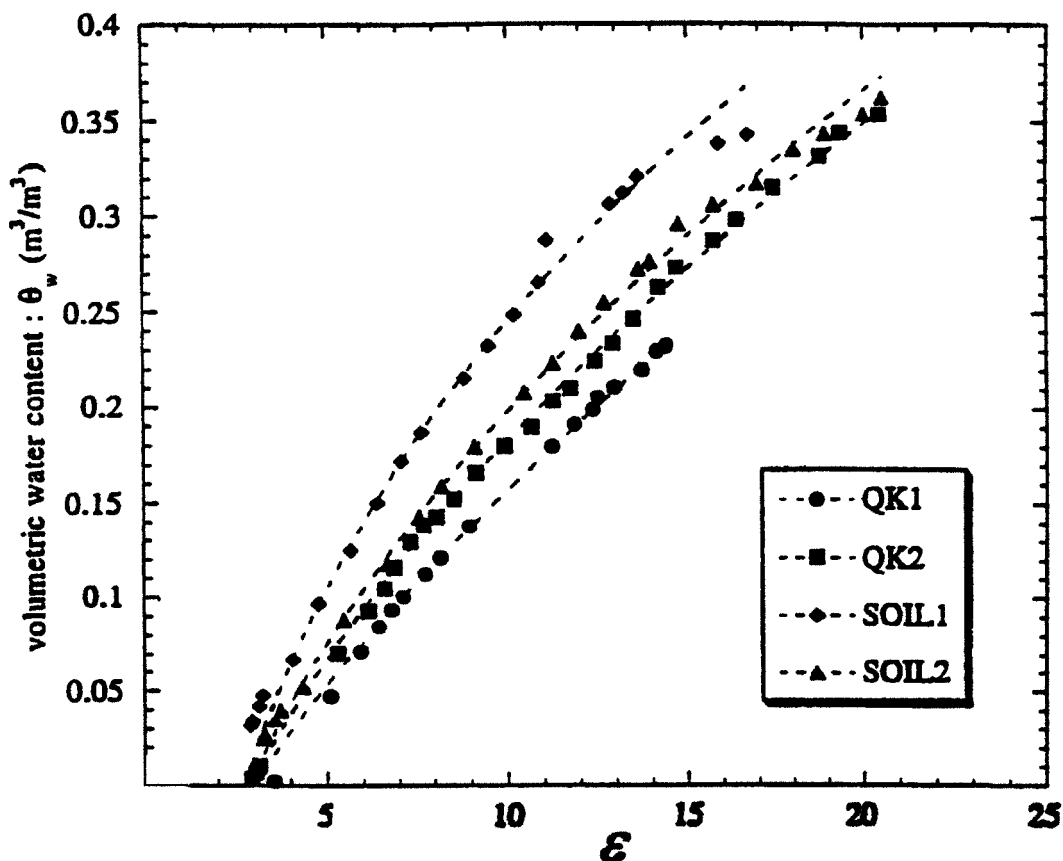


Fig. 2.13 Measured (symbols) and calculated (broken lines) dielectric constant for various soil samples versus water content θ_w at 22°C. Lichtenecker's formula (2.99) is applied for calculation. The characteristics of the samples (porosity ρ and the dielectric constant of the solid fraction are shown below. (Zakri et. al. 1998: With permission of J. Phys. D.: Appl. Phys., UK).

Sample reference	ε	Soil density	Bulk density	porosity
QK1	5.3	2.64	1.72	0.35
QK2	5.95	2.63	1.59	0.40
Soil 1	4.94	2.73	1.46	0.47
Soil 2	4.92	2.79	1.60	0.43

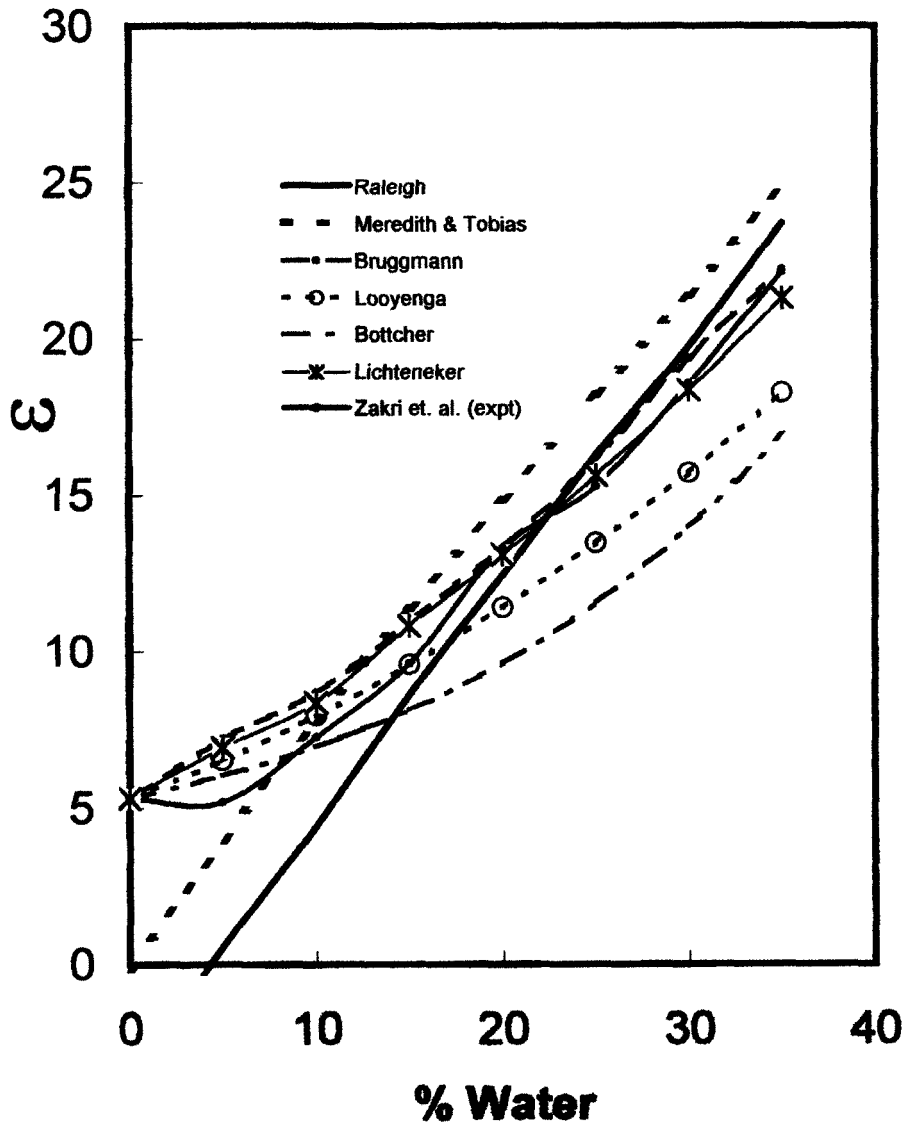


Fig. 2.14 Application of various formulas to soil sample QK1 and comparison with measured values (Zakri et. al. 1998: With permission of J. Phys. D.: Appl. Phys., UK). The calculations have been carried out for $\epsilon_{\text{water}} = 79.4$ and $\epsilon_{\text{soil}} = 5.3$. Agreement with Lichteneker's formula is much better than with others.

For parallel combination of dielectrics the dissipation factor is given by

$$\tan \delta = \frac{V_p \epsilon'_p \tan \delta_p + V_m \epsilon'_m \tan \delta_m}{V_p \epsilon'_p + V_m \epsilon'_m} \quad (2.110)$$

Morgan³⁰ has measured the dissipation factor in layers of dry kraft paper stacked together by compressive force of up to 350 kPa. The dielectric constant of cellulose at 20°C is 6.0-6.5 with a density of 1450 kg/m³.

Fig. 2.15 shows ϵ' and ϵ'' at various frequencies and temperatures. The dielectric constant decreases slightly with frequency except at higher temperatures and above 10 kHz there is a trend towards higher values. This anomalous dispersion has been observed in earlier measurements on Kraft paper. The effect of compressive force is to increase the dielectric constant as expected due to a decrease in thickness of the stack. ϵ'' increases slowly upto 1 kHz and more rapidly at higher frequencies. This is attributed to the Maxwell-Wagner effect. Calculation of ϵ' and ϵ'' by assuming series and parallel arrangement shows that series equivalent gives better agreement with the measured values after increase in density is taken into account for both arrangements.

2.12 DIELECTRIC CONSTANT OF LIQUID MIXTURES

A study of dielectric constant of liquid mixtures is important both from the points of view of dielectric theory and practical applications. Several formulas are available for the calculation of the dielectric constant of binary mixtures of liquids and a collection is given below. We denote the dielectric constants of the individual components by ϵ_1 and ϵ_2 , and that of the mixture by ϵ_m (Raju 1988, Van Beck 1967). The volume fractions are denoted by V_1 and V .

2.12.1 RALEIGH'S FORMULA

$$\epsilon_m = \epsilon_1 \frac{\frac{2\epsilon_1 + \epsilon_2}{\epsilon_2 - \epsilon_1} + 2V_2 - \frac{1.575(\epsilon_2 - \epsilon_1)}{4\epsilon_1 + 3\epsilon_2} V_2^{3.33}}{\frac{2\epsilon_1 + \epsilon_2}{\epsilon_2 - \epsilon_1} - V_2 - \frac{1.575(\epsilon_2 - \epsilon_1)}{4\epsilon_1 + 3\epsilon_2} V_2^{3.33}} \quad (2.111)$$

where the subscripts 1, 2, m refer to the two components and the mixture respectively.

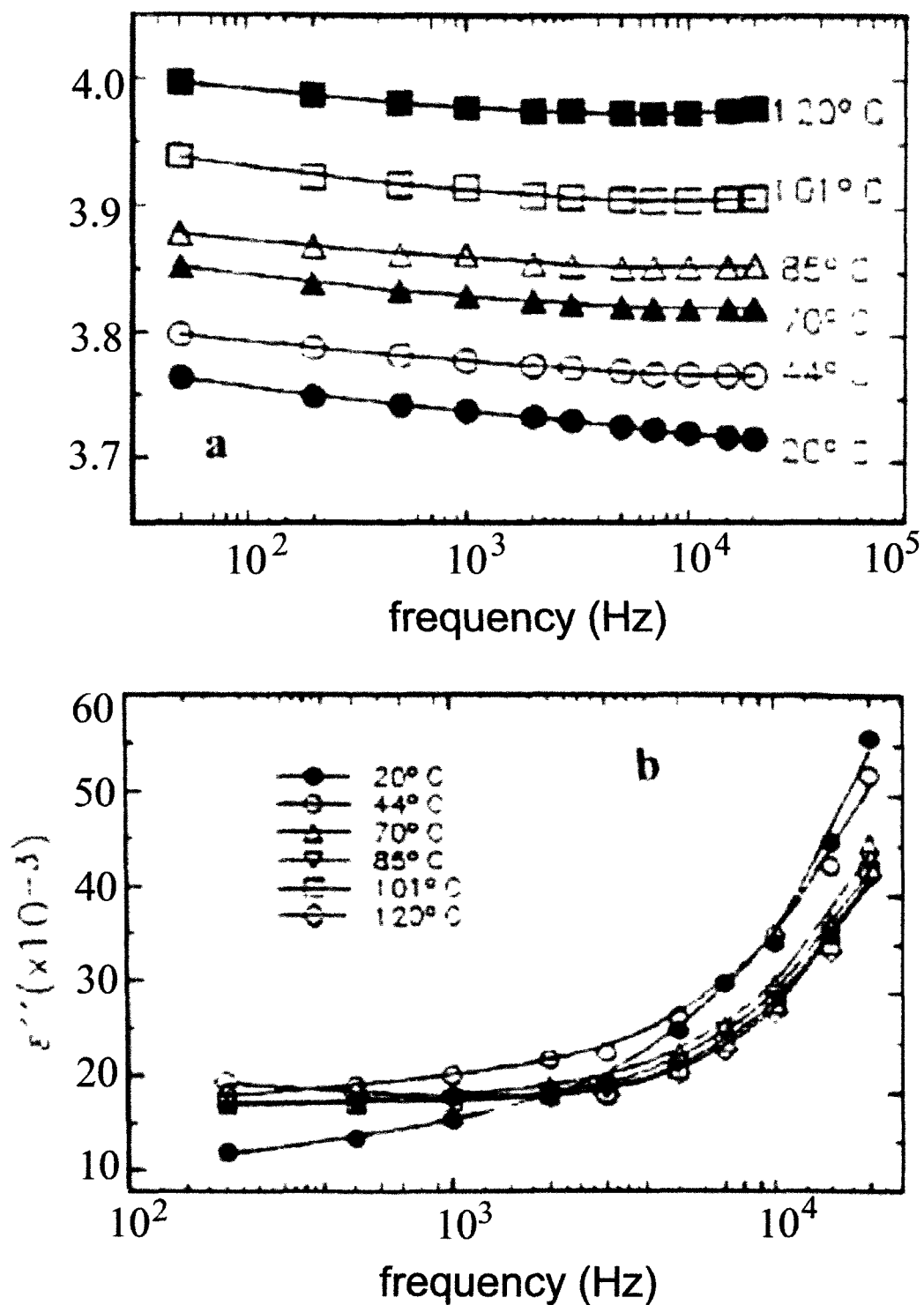


Fig. 2.15 Variation of complex dielectric constant in Kraft paper with frequency and temperature at a compressive stress of 336 kPa. (a) ϵ' (b) ϵ'' (Morgan, ©1998, IEEE).

2.12.2 FORMULA OF MEREDITH AND TOBIAS

$$\varepsilon_m = \varepsilon_1 \frac{A}{B}; \quad (2.112)$$

$$A = \frac{2\varepsilon_1 + \varepsilon_2}{\varepsilon_2 - \varepsilon_1} + 2V_2 - 1.277 \frac{2\varepsilon_1 + \varepsilon_2}{4\varepsilon_1 + 3\varepsilon_2} V_2^{7/3} \frac{1.575(\varepsilon_2 - \varepsilon_1)}{4\varepsilon_1 + 3\varepsilon_2} V_2^{10/3}$$

$$B = \frac{2\varepsilon_1 + \varepsilon_2}{\varepsilon_2 - \varepsilon_1} - V_2 - 1.277 \frac{2\varepsilon_1 + \varepsilon_2}{4\varepsilon_1 + 3\varepsilon_2} V_2^{7/3} \frac{1.575(\varepsilon_2 - \varepsilon_1)}{4\varepsilon_1 + 3\varepsilon_2} V_2^{10/3}$$

2.12.3 BRUGGEMAN'S FORMULA

$$\frac{\varepsilon_2 - \varepsilon_m}{\varepsilon_2 - \varepsilon_1} \left(\frac{\varepsilon_1}{\varepsilon_m} \right)^{1/3} = 1 - V_2 \quad (2.113)$$

where V_2 is the fractional volume of the second component.

2.12.4 LOOYENGA'S FORMULA

$$\varepsilon_m = \left[\varepsilon_1^{1/3} + V_2 \left(\varepsilon_2^{1/3} - \varepsilon_1^{1/3} \right) \right]^3 \quad (2.114)$$

2.12.5 BÖTTCHER'S FORMULA

$$\varepsilon_m = \varepsilon_1 + \frac{3V_2\varepsilon_m(\varepsilon_2 - \varepsilon_1)}{2\varepsilon_m + \varepsilon_2} \quad (2.115)$$

The last two formulas are symmetrical. Fig. 2.16 helps to visualize these formulas for a mixture of water and methyl alcohol with $\varepsilon_1 = 78$, $\varepsilon_2 = 32.50$ ³¹. Looyenga's formula has been proved to be applicable for this mixture³². The empirical formulas of Lichtneker, equation (2.99) and Bruggeman, equation (2.113) yield almost identical results while the formulas of Looyenga and Bottcher give values that are higher.

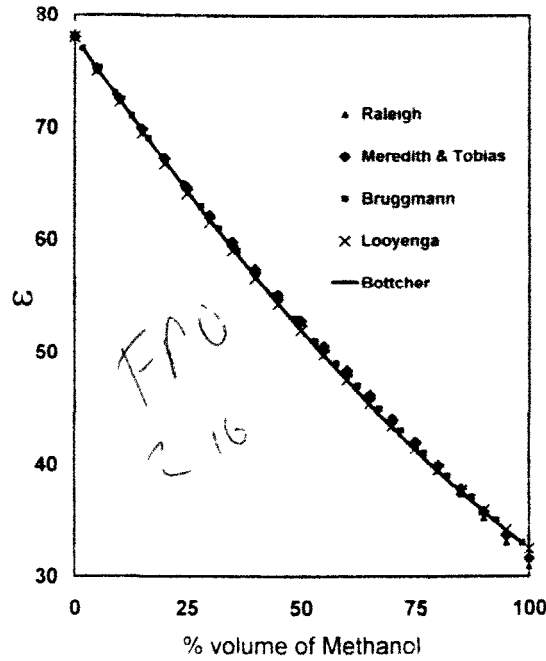


Fig. 2.16 Dielectric constant of mixtures of water and methanol according to various formulas. Looyenga's equation agrees with the measured values of Skai et. al.. (1995: With permission of American Physical Society).

All the formulas listed above are independent of temperature implying that they are applicable at the same temperature. If one wishes to calculate the dielectric constant of a mixture at any other temperature measurements on the individual components have to be carried out at that temperature.

The question has been examined by Govinda Raju (1988) in light of fundamental theories described in the earlier part of this chapter. According to the Debye theory the dielectric constant of a mixture of liquids is given by :

$$\frac{\epsilon_m - 1}{\epsilon_m + 2} = \frac{1}{3\epsilon_0} \sum_{i=1,2} N \left(\alpha_e + \alpha_a + \frac{\mu^2}{3kT} \right) \quad (2.116)$$

The quantities within the summation sign correspond to each component of the mixture. The Onsager equation for a mixture of liquids is given by

$$(\epsilon_m - n_m^2)(2\epsilon + n_m^2) = \sum_{i=1,2} \frac{N_i(n_i^2 + 2)^2 \mu_i^2}{9\epsilon_0 kT} \quad (2.117)$$

where n_m is the refractive index of the mixture given by equation (2.114) by substituting $\varepsilon = n^2$. It can also be calculated using equation (2.98) as an approximation. The calculation requires an iterative procedure. Good agreement is obtained between the measured and calculated values of ε .

2.13 EFFECT OF HIGH ELECTRIC FIELDS

Dielectric measurements are usually carried out at low electric field strengths, particularly if frequency is used as a variable. Tan δ measurements using **Schering Bridge** at power frequency are the exceptions. Dielectrics in power equipment are stressed to very high values and at threshold of partial discharges or breakdown, the electric field experienced by insulation can reach several hundred MV/m. Analysis of the change in ε due to high electric field takes into account the higher order terms in the Langevin function and the result shows that the dielectric constant decreases due to high fields. The decrease $\Delta\varepsilon$ may be expressed as³³ :

$$\Delta\varepsilon = -\frac{E^2 N_A \mu^4 C}{45V \varepsilon_0 (kT)^3} \quad (2.118)$$

where C is a constant and V the molar volume. The negative sign indicates that there is a decrease in the dielectric constant. C is given by

$$C = \frac{(\varepsilon + 2)^4}{81} \quad (2.119)$$

An alternative treatment due to Böttcher gives

$$C = \frac{(n^2 + 2)^3 \varepsilon^4}{(2\varepsilon + n^4)(2\varepsilon + n^2)(2n^2 + 1)} \quad (2.120)$$

where n is the refractive index. On the basis of Kirkwood theory a relatively simple equation has been derived:

$$\varepsilon \approx n^2 + \frac{N_A \mu (n^2 + 2)}{3\varepsilon_0 EV} \quad (2.121)$$

To get an idea of the influence of the electric field on the dielectric constant we substitute the values appropriate to water:

$N_A = 6.03 \times 10^{23}$, $n^2 = 1.8$, $\mu = 1.87 \text{ D} = 6.23 \times 10^{-30} \text{ Cm}$, $V = 18 \times 10^{-6} \text{ m}^3$, $\epsilon_0 = 8.854 \times 10^{-12} \text{ F/m}$, $E = 1 \times 10^9 \text{ V/m}$ gives 31.7 which is less than 50% of the measured static dielectric constant of 81. The decrease of the dielectric constant under high electric field strength has been generally neglected almost entirely in the literature on dielectric breakdown, high field conduction and partial discharges which can hardly be justified.

2.14 ATOMIC POLARIZABILITY

Atomic polarizability arises due to the displacement of the nuclei of atoms forming the molecule, relative to each other, in contrast with the electronic polarizability that arises as a consequence of electronic displacement, in an electric field. Whether a molecule possesses a permanent dipole or not, if it has polar bonds, as in the most cases of dissimilar atoms forming a molecule, the applied field induces a displacement; this displacement is superimposed on the electronic displacement discussed in section 1.3. Though atomic polarization exists in all molecules, it is more pronounced in molecules that have relatively weak bonds.

The charge displacement in an electric field involves changes in bond length and bond angle, in addition to bending or twisting of polar groups with respect to each other. The displacement is restricted by the degree of vibrational freedom of the molecule³⁴. Atomic polarizability does not have any simple relationship with electronic polarizability or orientational polarizability. For our purposes, it is sufficiently accurate to determine atomic polarization by the difference between the total polarization and the sum of electronic and orientational polarization. The atomic polarization is usually 1-15% of the electronic polarization, though in certain compounds it can reach a value of about 30% of the electronic polarization.

In the periodic table of elements a noble gas (He, Ne, Ar, Kr, Xe) separates an alkali metal (Li, Na, K etc) from a halogen (F, Cl, Br, I). If the alkali metal loses an electron or the halogen gains one, their electronic structure will be similar to the noble gas in which the outer shell is completely filled. The atom now becomes relatively highly stable. When an electron is added or removed the atom becomes a negative or positive ion. The force of attraction between oppositely charged ions results in an ionic bond. For example, in a molecule of sodium chloride the chlorine atom becomes a negative ion and the sodium atom a positive ion. As a result there will be a relative displacement of the

charge centers and the molecule possesses a permanent dipole moment. When there is no electric field the molecules are oriented at random and there is no net dipole moment.

Consider two molecules oriented parallel and anti-parallel to the external field. The molecule parallel to the field will be elongated with an increase in its dipole moment while a molecule anti parallel will have its dipole moment reduced. On average there will be a net contribution to the polarization which may be called as ionic or atomic polarization, depending upon whether the molecule is ionic or not. The polarizability is denoted by α_a and this contribution should be added to the electronic and orientational polarizability of the molecule. Thus we have for total polarizability

$$\alpha_T = \alpha_o + \alpha_a + \alpha_e$$

leading to

$$\mathbf{P} = NE_i \left(\alpha_e + \alpha_a + \frac{\mu^2}{3kT} \right) \quad (2.122)$$

The Clausius Mosotti function is obtained by replacing α_e by α_T in (2.23).

The average polarizabilities of halogen ions and alkali metal ions are given in Table 2.11, with the electronic polarizability of rare gas atoms included for comparison. Ionic polarizability is generally higher than the electronic polarizability.

Table 2.11

Average polarizability of halogen ions and alkali metal ions

HALOGENS ($\times 10^{-40}$ F m ²)		NOBLE GAS ATOMS ($\times 10^{-40}$ F m ²)		ALKALI METALS ($\times 10^{-40}$ F m ²)	
		He	0.22	Li ⁺	0.032
F ⁻	1.19	Ne	0.45	Na ⁺	0.26
Cl ⁻	4.0	Ar	1.84	K ⁺	1.0
Br ⁻	4.95	Kr	2.69	Rb ⁺	1.87
I ⁻	7.7	Xe	4.37	Cs ⁺	2.75

CRC handbook (1985-86).

Entries in the same row have the same electronic configuration. However the nuclear charge increases from left to right resulting in a decrease of the polarizability. This is attributed to the fact that the greater Coulomb force between the nucleus and the

electrons offers greater resistance to the electronic displacement. We conclude this section by summarizing the average polarizability of selected molecules (Table 2.12).

Table 2.12
Average Polarizability of selected molecules

Molecule	$\alpha_e (\times 10^{-40} \text{ F m}^2)$	Molecule	$\alpha_e (\times 10^{-40} \text{ F m}^2)$
CO	2.16	N ₂	1.89
Cl ₂	5.12	NO	33.3
CCl ₂ F ₂	8.67	O ₂	1.75
CF ₄	4.26	CO ₂	3.23
CH ₄	2.87	D ₂ O	1.40
CH ₃ O	3.65	H ₂ O	1.61
C ₆ H ₆	11.45	N ₂ O	3.36
D ₂	0.88	NH ₃	2.51
F ₂	1.52	SF ₆	14.65
H ₂	0.89	SeF ₆	7.91
HCl	2.92	SiF ₄	6.05

(CRC Handbook, 1986; with permission of CRC Press).

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